SPECIAL EDITION

TRANSACTIONS

of the American Society for Steel Treating

NITRIDING SYMPOSIUM

White Layer in Gun Tubes —*H. H. Lester*

The Iron-Nitrogen System —*Samuel Epstein*

Study of the Nitriding Process —*V. O. Homerberg and J. P. Walsted*

The Nitriding Process —*Dr. Adolph Fry*

Researches on Nitriding Steels —*O. E. Harder, J. T. Gow and L. A. Willey*

Investigations in Nitriding —*Robert Sergeson*

Short-Time Nitriding of Steel in Molten Cyanides —*A. B. Kinzel and J. J. Egan*

Practical Fundamentals of the Nitriding Process —*H. W. McQuaid and W. J. Ketcham*

Nitrided Steel in High Pressure Steam Service —*V. T. Malcolm*

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TO THE MEMBERS OF THE AMERICAN SOCIETY FOR STEEL TREATING

Recognizing the wide-spread interest in the process of nitriding and in steels for nitriding, your Society sponsored a symposium on this subject during the National Metal Congress in Cleveland, Ohio, on Friday, September 13, 1929.

In the ordinary course of procedure, the papers presented at this symposium as well as the discussions would reach the membership from time to time in TRANSACTIONS. However, this would not only cause delay in publication of the papers but the material would not be handy for reference. It therefore, has seemed to your Officers and Board of Directors that it would be rendering a distinct and timely service to the membership, to publish all of the papers and discussions presented at the Nitriding Symposium in one volume. This extra number of TRANSACTIONS has consequently been printed to provide a special service to the membership.

We take pleasure in expressing our deep appreciation and indebtedness to W. B. Coleman for the organization of the symposium; to Prof. George B. Waterhouse, chairman of the sessions; to the authors of the several papers; and to those who contributed to the discussions.

On behalf of the Officers and Board of Directors,

Zay Jeffries
President

W. H. Eisenman
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Cleveland, Ohio
October 15, 1929

Nitriding Symposium

HELD DURING THE ANNUAL CONVENTION OF
THE AMERICAN SOCIETY FOR STEEL TREATING
CLEVELAND, SEPTEMBER 13, 1929

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W. B. Coleman
Organizer of Symposium

THE WHITE LAYER IN GUN TUBES AND ITS RELATION TO THE CASE OF NITRIDED CHROMIUM-ALUMINUM STEEL

By H. H. Lester

Abstract

There is a hard surface skin, known as the "white layer", formed in the bore of gun tubes during service.

This layer seems to result from the effect of hot powder gases in contact with the gun steel at high pressures. It is concluded from metallographic and X-ray diffraction evidence that this layer is the result of nitrification of the bore surface.

The layer studied was found to be largely austenitic. The alpha and gamma lattices of the iron crystals were found to be enlarged by 0.5 and 0.6 per cent respectively. The alpha lattice of the iron crystals in the case of nitrided chromium-aluminum steels was found to be enlarged by 0.5 per cent.

It is suggested that this enlargement is due to the absorption of nitrogen and that most of the hardness of the case is due to the Fe-N solid solutions.

It is pointed out that the austenitic case of this gun tube merits further study as a possible extension of nitriding to other steels and for special services.

THERE occurs in the bore of a gun after firing a glass-hard surface skin usually called the "white layer". The nature of this layer has been the object of many investigations and there is extensive experimental data with regard to it. The present paper contributes some additional data and points out similarities of this layer with the nitride case of nitrided chromium-aluminum steels. It is thought that these data may have a bearing on the better understanding of the nature of nitride cases in general.

Materials

The "white layer" data were obtained from a section of a trepanned ring from a 12-inch gun, Model 1895, a former study of which was reported to the Ordnance Office in 1912. This ring

The author, H. H. Lester, member of the society, is research physicist, Watertown Arsenal, Watertown, Mass. Manuscript received July 29, 1929.

was taken from the bore of the gun well beyond the region of maximum erosion. The data on nitrided chromium-aluminum steel were obtained from a portion of a 50-caliber machine gun barrel made from this steel that had been nitrided and tested to destruction. This barrel had been nitrided both on the bore surface and on the outer circumference.

Metallographic Tests

Figs. 1, 2, and 3 show typical conditions of the bores. The hard surface is broken up into a network of fine cracks. The network is larger near the breech than at the bore and is larger with large caliber than with small caliber tubes. It may be noted that the outward appearance of the 12-inch bore is very similar to that of the smaller tube except that the mesh of the crack system is of a different order of magnitude. The thickness of the hardened layer is also of a different order of magnitude, consistent with the size of the bore.

Figs. 4 and 5 show sections through the white layer of the larger gun. This layer does not respond readily to etching reagents. On prolonged immersion it tends to stain, becoming yellow, changing to blue on longer exposure, and to dark blue or black on still longer exposure to an alcoholic solution of nitric acid. Similar color changes were found to occur with the nitrided case of the bore of the smaller gun. The coloration is fairly uniform except that uncolored ferrite grain boundaries may be seen projecting into the hard layer. The structure developed, except for the color effects, at low magnifications, resembles a fine-grained sorbite.

As shown below, however, the case contains a large percentage of austenite, and the sorbitic appearance disappears on higher magnification, as illustrated in Fig. 6.

In other studies of the white layer, careful etching has in some cases developed a martensite structure. Langenberg, in a study of rings from a 10-inch gun, found martensite. In the previous report on the present material, and in the majority of studies that have been made on other barrels, no martensite structure could be developed. The writer was unable to get any typical martensite structure in the present instance.

Fig. 6 illustrates the structure developed under high magnification. This material might, perhaps, be called a mixture of austenite and troostite, but hardly martensite. Inasmuch as martensite struc-

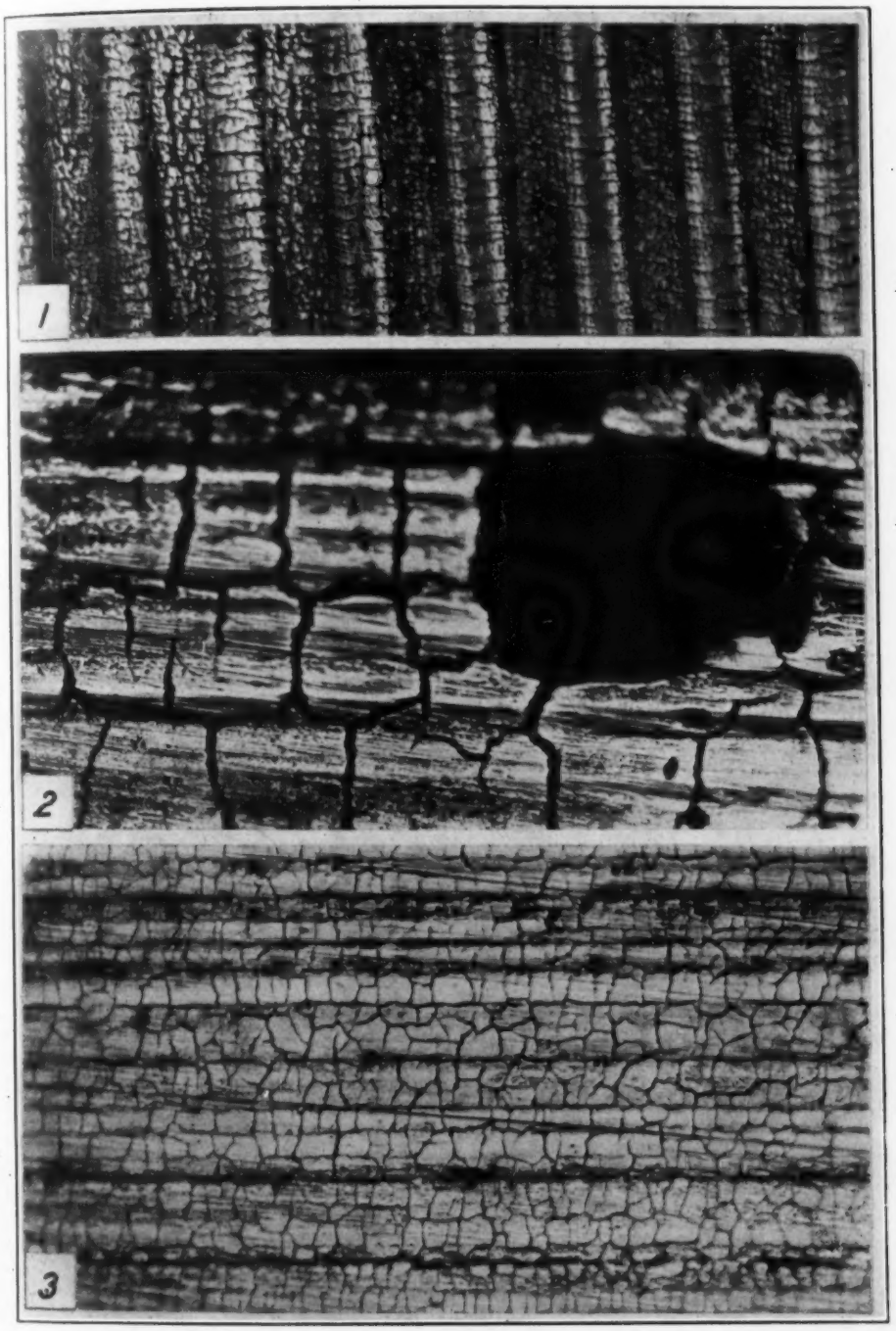

Fig. 1—Section of Trepanned Ring Taken from Bore of 12-Inch Gun. Photographed at Natural Size.
Fig. 2—Portion of Bore of 50-Calibre Machine Gun Barrel. × 100.
Fig. 3—Portion of Bore of 50-Calibre Barrel Near Muzzle. × 100.

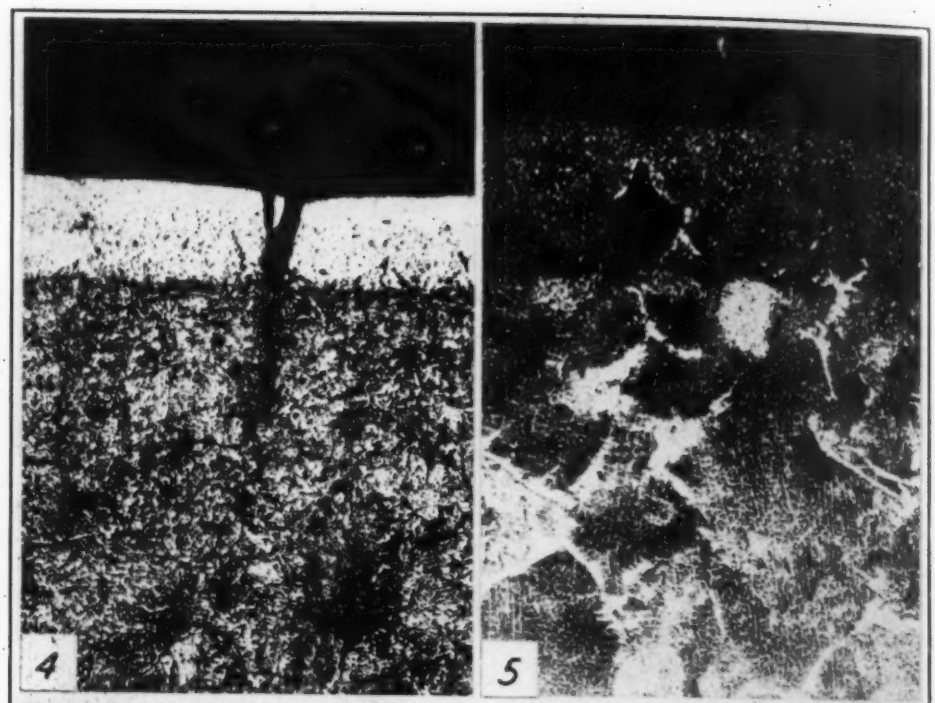

Fig. 4—Section Through White Layer of 12-Inch Gun. × 100.
Fig. 5—White Layer after Prolonged Etching. Note Ferrite Grain Boundaries Appearing in the Layer. × 200.
Fig. 6—Typical View of White Layer at High Magnification. × 3350. The Black Band at Bottom Marks the Junction of the White Layer with the Base Metal.
Fig. 7—Troostite Boundary Between White Layer and Base Metal. × 3350.

tures are often found in the white layer, it may be pointed out that such structures could result from the decomposition of austenite. X-ray evidence shows the structure of the material of the present tests to be largely austenite. It might have been martensite under different conditions of formation. Fig. 6 shows also the narrow black band that follows the hard layer. This is illustrated better in Fig. 7. This band suggests troostite. Beyond this troostite band, there may be seen, after prolonged etching, a broader darkened band that suggests sorbite.

Fig. 8 shows a section through the outer surface of the nitrided 50-caliber rifle barrel. This section was taken from the breech end of the barrel in the outer wall of the cartridge chamber. It shows a normal nitride case.

Fig. 9 is from the interior walls of the cartridge chamber. This chamber is protected from powder gases, but no doubt becomes heated. The case here is not quite normal, inasmuch as there is an innermost edge that does not etch readily.

Fig. 10 is from the region of maximum erosion, a surface view of which is shown in Fig. 1. A well developed white layer is quite evident. This layer, on light etching, tends to remain bright. On more prolonged etching it seems to stain, going through the same color changes found in the white layer of the 12-inch gun. In spite of the staining, however, structure is developed which contains occasional indications of acicular martensite needles, but for the most part there is little resemblance to martensite. In comparing Figs. 8, 9, and 10, one may note a steady growth of the light surface band. One may note, also, in the last picture that the outer layer, which we will refer to as the martensite layer, tends to crack along the boundary between the martensite and the troostite. This is not at the bottom, but, rather, at the middle of the nitride case.

The three figures under consideration represent three sets of conditions, two of which differed little, except that the second had been subjected to somewhat higher temperatures than the first. The third had been subjected to high temperatures, sudden fluctuations in temperature, and to the action of powder gases under pressure, which contain a large percentage of nitrogen. Following up the suggestion of Fig. 10, the specimen from which Fig. 9 was taken, was heated to 1000 degrees Fahr. and quenched in water. The result of this treatment is shown in Fig. 11. Where before there were no sharp lines of demarcation in the case, and where before

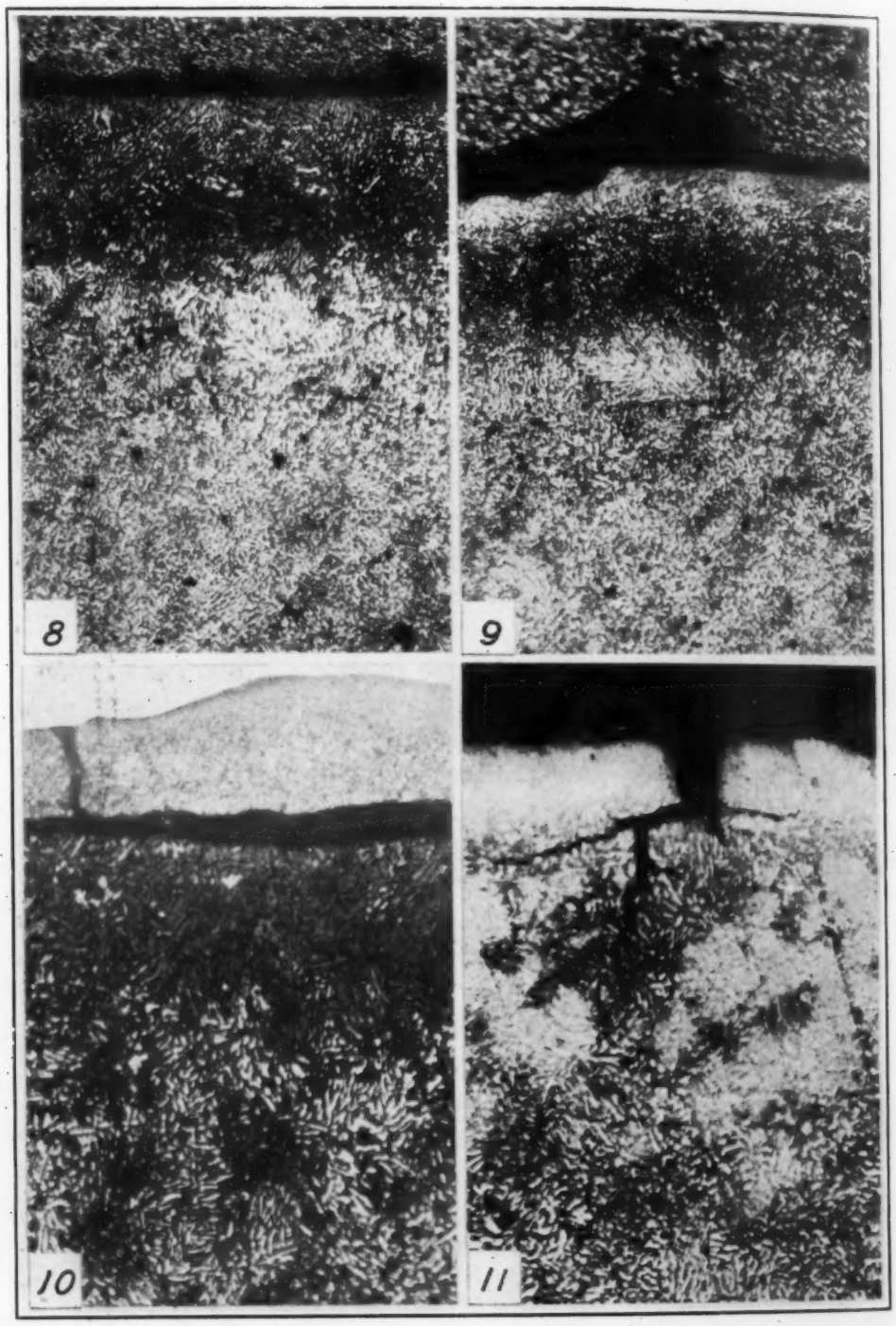

Fig. 8—Nitride Case from Outer Surface of 50-Calibre Rifle Barrel. × 100.
Fig. 9—From Inner Surface of Cartridge Chamber. This Part of the Metal is Protected from Powder Gases. × 100.
Fig. 10—Nitride Case of Fig. 9 from Region of Maximum Erosion. × 200.
Fig. 11—Nitride Case of Fig. 10 after Quenching from 1000 Degrees Fahr. × 500.

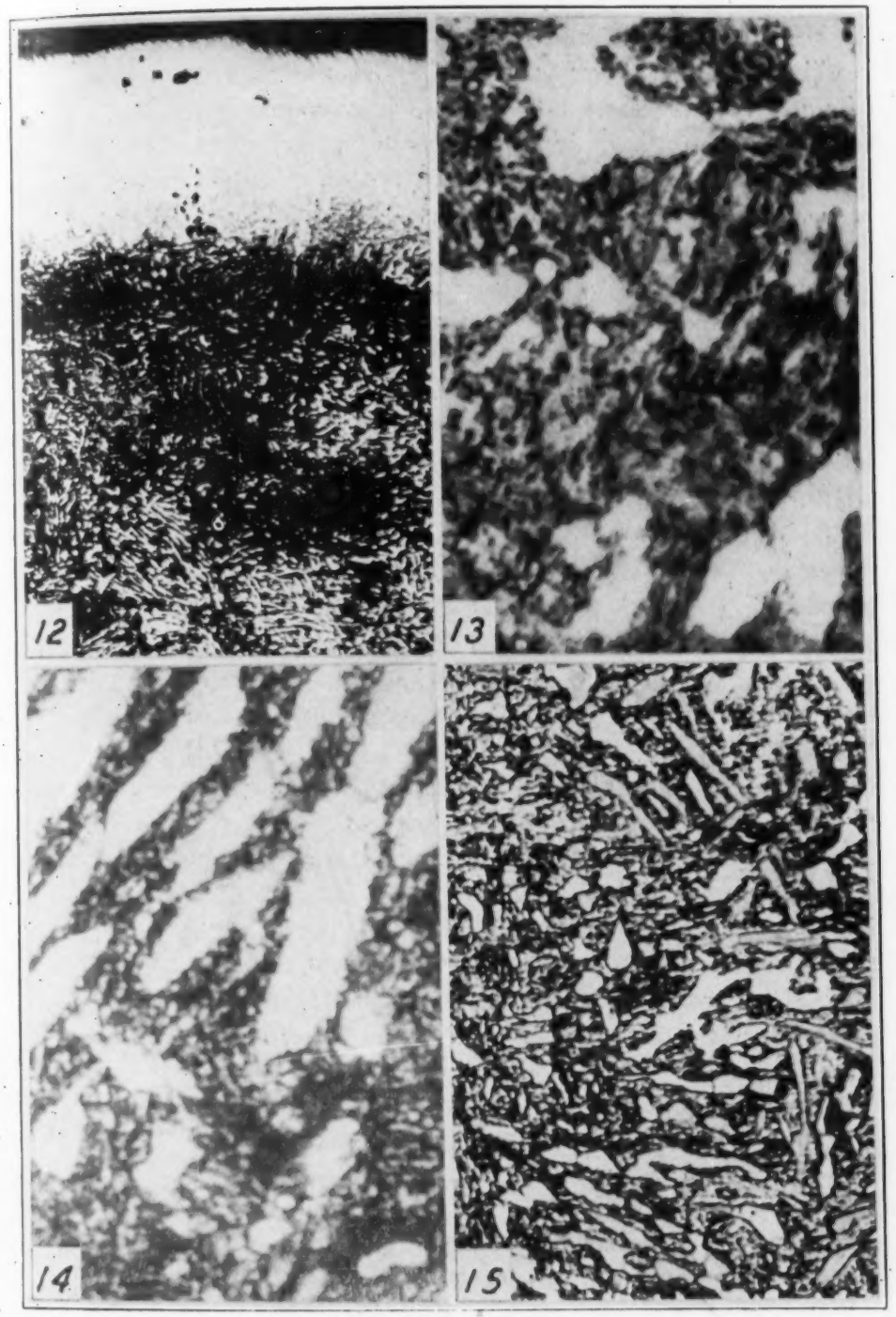

Fig. 12—Specimen of Fig. 11 After Quenching from 1000 Degrees Fahr. × 200.
Fig. 13—Specimen of Fig. 12 After Quenching from 1000 Degrees Fahr. Very Near Outer Edge of Case. × 3350.
Fig. 14—Specimen of Fig. 12 After Quenching from 1000 Degrees Fahr. About Middle of Outer Layer of Nitride Case. × 3350.
Fig. 15—Section from Bore Near Muzzle End After Quenching from 1200 Degrees Fahr. × 1000.

the case etched with relative ease, there now appears a sharply defined cleavage line, and the outer layer of the case does not etch readily at all. It behaves now like the specimen from the region of maximum erosion, and seems to have a martensitic outer layer separated from a sorbitic inner layer by a narrow band of troostite. The specimen was repolished and re-etched, and the effect developed even more strikingly in Fig. 12. Prolonged etching caused the colorations mentioned above, but developed structures. These are shown in Figs. 13 and 14. The structures found differ little from those of the unnitrided parts of the metal, although near the extreme edge, Fig. 13, the ferrite masses seem to be considerably broken up.

Material from near the muzzle end of the barrel, where the white layer-like formation was relatively small, was quenched from 1200 degrees Fahr. The strongly marked white layer was developed by this treatment, showing, perhaps, even more brilliant contrast with normal etchings than was found in the previous case. The structure close to the "outer" edge of the white layer is illustrated in Fig. 15. A peculiarity of this picture that may not appear readily in the reproduction, but that was quite marked on the ground glass of the camera, is that the ferrite masses show color variations. That is, some were brilliantly white, others were a slate gray.

Fig. 16 shows the structure near the middle of the outer layer. The ferrite masses are smaller than in the body of the metal, but otherwise are little changed in appearance.

Fig. 17 shows a troostite band that separates the outer layer from the rest of the case. It is quite similar to the band found in the white layer of the 12-inch gun.

In view of the other similarities, it would seem that the outer layer of the region of maximum erosion is probably the result of temperature fluctuations. It would also seem that probably the white layer of the gun is itself a quenched nitride case.

Before leaving the subject of metallographic tests, another interesting observation should be recorded. The outer circumference of the breech end of the rifle barrel is threaded. One section was cut perpendicular to the axis of the gun, and ground to expose the case near the tip of one of the threads. The results are illustrated in Fig. 18.

This white layer is quite different from those considered above. It could not be etched at all, nor even stained. It was very hard and tended to flake off in polishing. It contained in some cases

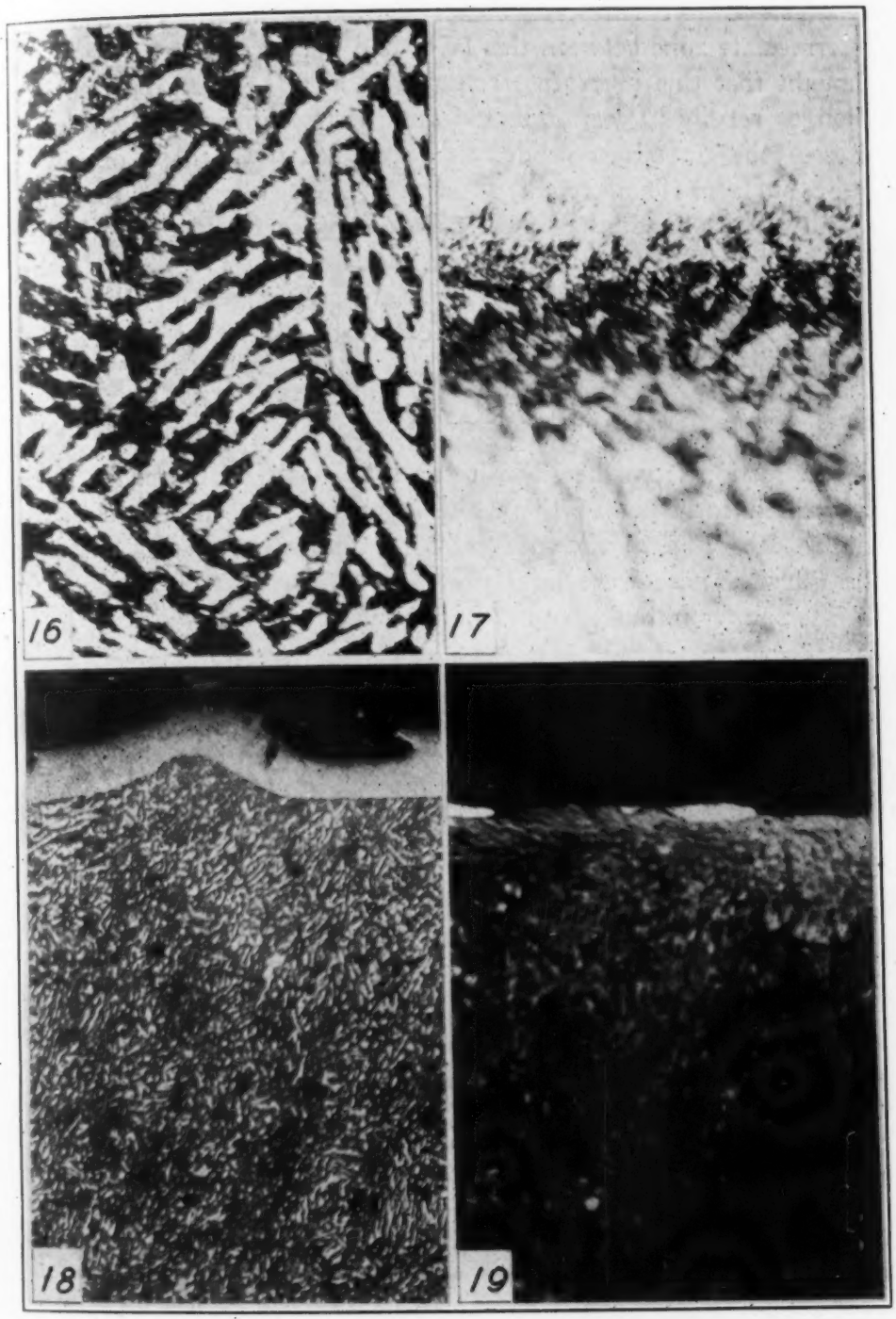

Fig. 16—Section from Bore Near Muzzle. Structure Near the Middle of the Outer Portion of the Case. Quenched from 1200 Degrees Fahr. × 1000.

Fig. 17—Section from Bore Near Muzzle. Quenched from 1200 Degrees Fahr. Troostitic Band at Junction of Outer Layer with Rest of Case. × 1000.

Fig. 18—Section from Threaded Portion of Gun Tube. This Layer did not etch and was very hard. It Spalled off Readily. × 100.

Fig. 19—From White Layer of 12-Inch Gun. Small Masses of White Material Similar to that of Fig. 18. These Adhere to the White Layer. × 500.

relatively large cavities and blister-like excrescences. There was no intermediate zone between this layer and the normal structure. It is thought that this represents actual iron nitride. Decarburized iron changes readily to one or both forms of iron nitride. Possibly the tips of the threads were decarburized, and their shape offering a large surface for nitrogen absorption, caused a super saturation of nitrogen. Portions of such a deposit were found in the 12-inch gun. Fig. 19 shows such masses adhering to the deeply etched section of the white layer. The relative resistance to the etching reagent is illustrated by the strong contrast between these masses and the white layer.

X-Ray Tests

A section from the 12-inch gun tube was used to get the X-ray diffraction spectrum of the white layer. A typical film is shown in Fig. 20. Fig. 21 shows a graphical analysis of the iron lines of the films. There were lines present that may have belonged to a nitride spectrum, but were too faint for accurate measurement. The

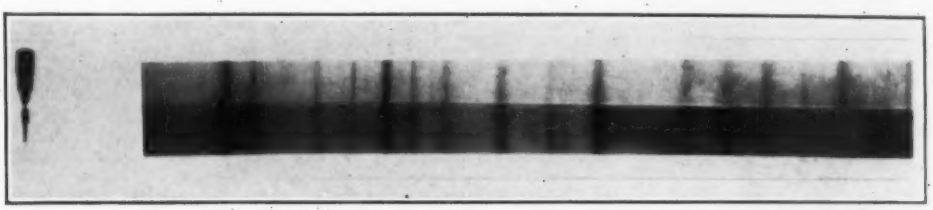

Fig. 20—X-ray Diffraction Spectrum of the White Layer of a 12-Inch Gun Tube. See Fig. 21.

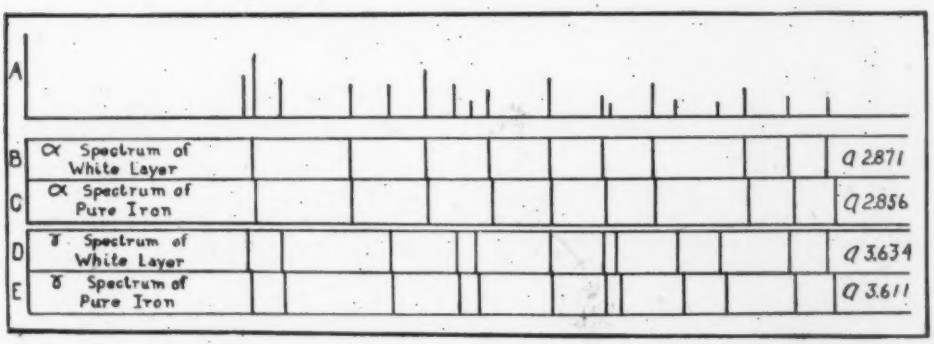

Fig. 21—A. Drawn from Film Shown in Fig. 20. Heights of Lines Represent Relative Intensities.
B. α lines of white layer.
C. α lines calculated from lattice for pure iron.
D. γ lines of white layer.
E. γ lines calculated assuming cube edge = 3.611.

principal lines belong to the two iron spectra, those of alpha and of gamma phases. In both spectra the lines were very diffuse and were displaced from normal positions by amounts indicating lattice extensions of 0.5 per cent for the alpha and 0.6 per cent for the gamma lattice.

Similar spectra were obtained for specimens from the bore and outer case of the machine gun barrel, and from a nitrided plate picked up in the laboratory. No differences were noted between the spectra from the bore and from the outer circumference of the gun barrel. The various results are collected in Table I.

Table I
X-Ray Diffraction Data

12-Inch Gun Alpha Lines	Machine Gun Alpha Lines	Nitrided Plate Alpha Lines	Calculated from A=2.856	For 12-Inch Gun
2.04	2.04	2.04	2.019	A=2.871
1.44	1.44	1.44	1.428	
1.170	1.170	1.168	1.165	
1.016	1.015	1.020	1.011	Lattice Enlargement 0.5%
0.908	0.907	0.910	0.902	
0.831	0.828	0.829	0.824	For machine gun
0.767	0.767	0.765	0.763	A=2.871
0.677	0.676	0.675	0.673	Lattice Enlargement 0.5%
0.641	0.641	0.642	0.638	
0.612	0.612	0.612	0.608	For nitrided plate A=2.874 Lattice Enlargement 0.5%
Gamma Lines				
2.10	.....	.....	.....	For 12-Inch Gun
1.82	.....	.....	.....	A=3.634
1.284	.....	.....	.....	From Measurement on
1.095	.....	.....	.....	Austenitic
1.050	.....	.....	.....	Steel
0.908	.....	.....	.....	A=3.611
0.831	.....	.....	.....	
0.812	.....	.....	.....	
0.741	.....	.....	.....	
0.699	.....	.....	.....	
0.641	.....	.....	.....	Lattice Enlargement 0.63%
0.612	.....	.....	.....	

The table gives values of interplaner spacings in Angstrom units. The values recorded are averages from several films. It may be noted that the alpha spectra for the two nitrided cases, and for the 12-inch gun white layer, are practically identical, and all show a lattice enlargement of approximately 0.5 per cent. The fourth column shows values calculated from the space lattice of pure iron, the edge of the cubic unit crystal being taken as 2.856.

No gamma spectra were found for the nitrided chromium-aluminum steel, although faint lines were present that may have

represented nitrides. The gamma spectrum of the 12-inch gun tube was almost as strong as the alpha spectrum. It is estimated that probably 40 per cent of the iron is in the gamma phase. That is, there is 40 per cent of austenite in the white layer as found in these tests. The displacements of the spectrum lines and their diffuseness would result if nitrogen were in solution in the iron.

Discussion of Results

The metallographic evidence shows that there is a strong similarity between the cases of nitrided chromium-aluminum steel and the white layer found in gun tubes. This similarity is more striking after quenching the nitride case.

The etching characteristics of the white layer and of the quenched nitride case, suggest solid solutions. The X-ray evidence for both is strongly suggestive of solid solutions. The writer feels that the evidence is sufficient to justify the conclusion that solid solutions do exist in these surface layers. There might be a question as to the nature of the solute.

In the case of the white layer, H. E. Wheeler has advanced a theory,[1] based on experimental evidence, which regards the white layer as, "An austenitic case caused by the alloying effect of nitrogen, with consequent lowering of the Ar_1 point to such an extent that the solid solution phase is formed on the surface." The present tests are in harmony with this theory. Various others have considered nitrogen in solution as the cause of the hardness of the white layer. Zimmerman[2] quotes Prof. Richards as stating that a few hundredths of 1 per cent of nitrogen (in solution) would have as much effect on the steel as several per cent of some other alloy. W. W. De Sveshnikoff[3] made actual determinations of carbon and nitrogen concentrations in the white layer of machine gun barrels, and found that in a nickel steel similar to that of the gun studied in the present investigation that the nitrogen content increased from 0.008 per cent in the original steel to 0.05 per cent at a point within

[1]H. E. Wheeler, "Nitrogen in Steel and the Erosion of Guns," *Journal*, Mining and Metallurgy, No. 160, 1920. "The Nitrogen Theory of Erosion", *Army Ordnance*, Vol. V, No. 30, 1925.

[2]Zimmerman, "Old and New Theories in Gun Erosion," *Army Ordnance*, Vol. V, No. 30, 1925.

[3]Sveshnikoff, "Carburization as a Factor in the Erosion of Machine Gun Barrels," *Army Ordnance*, Vol. 5, No. 30, 1925.

the case, and to 0.039 per cent at a point near the surface of the layer.

It should be remarked that his method of determination depended on dissolving nitrides, and that his measurements probably did take into consideration nitrogen in solution. The writer has not succeeded in finding reliable data on total nitrogen contents of the white layer.

The X-ray evidence indicates the possible presence of nitrides. No doubt, the presence of these in very small particles is a contributing cause of the hardness. It seems very probable, however, that the very large lattice distortion is a much more potent factor. This lattice distortion seems explicable only on the assumption that nitrogen was in solution in the iron. De Sveshnikoff showed, also, a marked absorption of carbon, the carbon content increasing from 0.33 to 0.48 per cent. However, this is still well below eutectoid proportions, and is not sufficient to account for the great hardness of the white layer, especially, whereas in the present investigation the layer is largely austenitic. The argument for carbon hardening would be strengthened if the layer were truly martensitic.

In view of Sveshnikoff's work it is probable that in the present study, the austenite was not saturated with carbon, and from the carbon argument should have been relatively soft. As a matter of fact it is glass hard. There seems no escape from the conclusion that nitrogen in solution, in ferrite and in austenite is responsible for the very great hardness of the white layer.

The argument for the hardness of the ordinary nitrided chromium-aluminum steel is similar. No gamma phase was found. The machine gun is subjected to high bore temperatures but, due to rapidity of fire and a smaller mass of metal, it is probable that there is no opportunity for the exceedingly rapid cooling necessary for the retention of austenite. True martensite could be expected, and occasional traces of it were found. It seems probable that in this, as in the ordinary white layer, the lattice distortion contributes more to the hardness than any other single factor. This distortion probably resulted from the absorption of nitrogen.

The results of the quenching experiments are suggestive. By some means quenching from 1000 and from 1200 degrees Fahr. made the nitride case very similar to the white layer in its reaction to etching. There was no perceptible change in the hardness. While experimental evidence is lacking, it is suggested that, perhaps, at the

elevated temperature, there was a diffusion of nitrogen and absorption of this by iron crystals deeper in the case.

X-ray data showed no additional lattice distortion, in fact, showed less if any change could be determined. This fact is not inconsistent with the above view, since the X-ray spectrum came from the outer edge of the case, and not from the inner portion. It is probable that the outer surface would lose nitrogen to the interior.

The above study is important, mostly in suggesting the effect of the solution of nitrogen in steel as one of the principal factors in hardening.

The writer feels that the effect of quenching merits additional study. Also, the formation of austenitic cases, and the physical properties of these, seem to warrant investigation. While no exact data were obtained, it was noticed that in breaking through the white gun layer, it seemed more tenacious than the nitride case and it did not seem to spall off at all in guns, although the ordinary chromium-aluminum steel case spalled badly. Possibly such cases would be superior for some services.

The writer is indebted to Col. T. C. Dickson, Commanding Officer, for sustained interest in this investigation and for permission to use the Arsenal facilities in the carrying out of the experimental work. Thanks are due, also, to Capt. G. J. Schaldt of Picatinny Arsenal for obtaining part of the X-ray data; to Miss M. R. Norton and to Mr. F. L. Brackley for material assistance in preparing illustrations and data.

DISCUSSION

Written Discussion: By V. O. Homerberg, Massachusetts Institute of Technology, Cambridge, Mass.

Dr. Lester's valuable contribution will settle, to a great extent, the controversy which has prevailed for a long time as to the exact character of this white layer.

Dr. Fay in his discussion of De Sveshnikoff's[1] paper explains the formation of the white layer as follows:

1. A hard layer, martensitic or troostitic in character, will be found in those parts of the gun which have been suddenly heated above Ac_1.

2. The formation of this hard layer will be accelerated by cold working the metal, the absorption of nitrogen, and of carbon.

[1]De Sveshnikoff "Carburization as a Factor in the Erosion of Machine Gun Barrels," *Army Ordnance*, Vol. 5, No. 30, 1925.

Many of the observations of the author are in agreement with the views set forth by Dr. Fay. In addition, Dr. Lester has called attention to the presence of nitrogen in solid solution in gamma iron, evidence of which he has obtained by X-ray examination. Although the author considers the lattice distortion to be due to the solution of nitrogen in iron, is it not possible that the cold working of the metal may also act as a contributing factor?

I am pleased to note that the white case obtained at the tip of the threads in the breech end of the rifle barrels is considered to be iron nitride. This statement is in accord with observations made in my laboratory with regard to the white surface layer which sometimes occurs in nitrided specimens. The solution of nitrogen in steel is considered as the principal factor to account for the extreme hardness of the white layer. Is this nitrogen present as such, or as one or more nitrides? I presume that this point is just as difficult to answer as the question of the form of carbon in gamma iron in steel. It seems to me that it would be very difficult to determine definitely whether nitrogen as nitride is in solution or in a fine state of dispersion. I should like to know whether or not it is possible to answer this question.

A very important suggestion is made relative to the formation of austenitic cases. An investigation into the nitriding of austenitic materials should prove interesting. The addition of nickel to the present nitriding steels offers possibilities. Although the presence of this element has been considered as one retarding the nitriding action, the question has not received the study which it warrants. This problem is being investigated in my laboratory at the present time.

Written Discussion: By John P. Walsted, Massachusetts Institute of Technology, Cambridge, Mass.

Dr. Lester calls attention to the formation of gamma iron on nitriding a steel. That the white layer is due to the formation of austenite, there can be no doubt. Dr. Lester also mentions the occurrence of lines in the X-ray spectrum that are possibly nitrides. These lines have also been found in our work at the Massachusetts Institute of Technology. As yet no attempt has been made to measure this pattern. When speaking of the white layer of nitrided specimens, it is well to bear in mind that at the outside of the case there is often noticed a very thin brilliant layer that does not etch. Inside this layer is a zone which is nearly white and in which carbide particles seem to disappear. The outer layer I believe to be nitride, the second zone I believe to be the austenite.

Author's Closure

The work of Dr. Fay, referred to by Dr. Homerberg, was done partly, I think, on the very same 12-inch gun that furnished material for the present study. His idea that cold work effects were partly responsible for the hardening of the bore surface seem to be in error.

The metal on the extreme inner surface is heated not only above the Ac_1 point, but actually above the fusion point, and is blown out as liquid metal. Under these circumstances it is difficult to consider cold work effects in which the metal must be at least below the A_1 point.

With regard to the solution of nitrogen it is, perhaps, difficult to say whether nitrogen is dispersed in the solvent as nitrogen or as nitrides. It seems to the writer to make little difference. The same question comes up in considering the dispersion of carbon. So far as the writer is aware there is no test that can be applied that would really settle the matter. We have in effect a solution of nitrogen. In a supersaturated solution it seems to the writer that a nitrogen atom is apt to form close bonding with sufficient adjacent iron atoms to form a nitride molecule. This group of atoms occupying the region in the space group normally occupied by an equivalent number of iron atoms would be possible and would, perhaps, account for observed lattice distortion. According to this view there would be a fine dispersion of nitride molecules in the ferrite or in the austenite, but the lines of demarcation between this and a true solid solution would be rather indefinite. Of course part of the nitrides are no doubt precipitated and exist as segregated masses of iron nitride, though possibly of subcritical dimensions, as far as X-ray tests are concerned.

As to the question of the influence of nickel on the absorption of nitrogen Ruder and Brophy* found that nickel has no influence in retarding the absorption of nitrogen. It does, however, tend to stabilize austenite and, when present in sufficient quantity, perhaps, makes possible an austenitic nitride case where otherwise the case would be ferritic.

In reply to Dr. Walsted, the writer would be interested in comparing X-ray spectra Dr. Walsted mentions with his own. It should be remarked that tests on pure iron wire that was nitrided in accordance with the technique usually employed in treating aluminum steels gave no evidence of austenite. There were two or three spectra present, one of which seemed to belong to a face-centered lattice, but it was different from the spectrum of austenite. One spectrum obviously belonged to a hexagonal structure.

It is planned to determine these structures more accurately at a later time. No iron spectra were found at all, indicating complete transformation of the iron to two nitrides. The third spectrum may have been due to iron oxide or to a third nitride.

X-ray tests on various nitrided aluminum steels gave no indication of austenite. No doubt Dr. Walsted has experimental evidence for his view that the light layer adjacent to the thin layer of iron nitride in such steels is austenitic. The writer has, however, found no such evidence in his own experiments.

Lest he be misunderstood with reference to the austenitic case found in this particular study the writer desires to state that in his opinion the white layer of the gun tube may be austenite, or it may be martensite, or

*W. E. Ruder and G. R. Brophy, *Chemical and Metallurgical Engineering*, Nov. 9, 1921.

possibly even troostite, depending upon circumstances of its formation. The interesting point in this connection is that the austenitic case may occur. It should be borne in mind that powder gases responsible for white layer formations carry not only nitrogen, but carbon. The metal of the tube surface when in the austenitic state would absorb both carbon and nitrogen. Both elements probably contribute to the hardness.

In this connection attention should be called to a very interesting and instructive paper presented in 1921 by W. E. Ruder and G. R. Brophy,* in which they call attention to the simultaneous absorption of carbon and nitrogen and to the similarity of carbon and nitrogen in producing hardness in steel. They tested various alloy steels with regard to their ability to absorb nitrogen and among these, steels of varying nickel contents. It is interesting to note that for a 3 per cent nickel steel of similar composition to the steel of the 12-inch gun of the present study they found a decided difference in the nature of the case formed over that for lower nickel contents. To quote from their paper in reference to this point, "The change in metallographic appearance, that is disappearance of needles and large dark patches—is partly due to reduction in grain size, but examination under high power discloses an entire change in structure—indicating that nickel increases the solubility of the ferrite for nitrogen and what carbon there is present." This paper came to the attention of the writer after his own paper was delivered. It would seem that Ruder and Brophy probably developed an austenitic case. It would seem also that a condition for such a case is a critical content of an alloy such as nickel that tends to stabilize the austenite.

*See foot note on opposite page.

OBSERVATIONS ON THE IRON-NITROGEN SYSTEM

By Samuel Epstein

Abstract

By means of thermal analyses, microscopic examinations and X-ray analyses of nitrided electrolytic iron specimens, a study has been made of the iron-nitrogen system. From the data obtained and with the two existing diagrams of Sawyer and Fry as a basis, a modified iron-nitrogen constitution diagram has been tentatively drawn. The upper temperature horizontal noted by Sawyer was also observed but this has been ascribed to a peritectoid instead of a eutectoid transformation. Three nitrided layers were observed, whereas Fry noted only two. The three layers have been designated as Fe_2N, Fe_4N, and Fe_8N. Observations on several specimens of aluminum-molybdenum nitriding steel are also described.

I. Introduction

FROM the standpoint of nitriding, the constitution diagram of the iron-nitrogen system is important, mainly because it must form the basis of our understanding of the more complex system involved in the nitriding of the special alloy steels. No practical use has been made, or is likely to be made, of nitrided pure iron. The iron-nitrogen system may be divided into two parts, one of a low nitrogen content corresponding with the core of nitrided articles, and one of a much higher nitrogen content, corresponding with the case.

The low nitrogen side of the diagram is of general importance since it is believed that comparatively small amounts of nitrogen may materially affect the mechanical properties of iron and steel. According to the diagram as determined by Fry[1], the iron nitride constituent, familiar to metallographers in its characteristic needle form, is appreciably soluble in iron in the temperature range 500-550

[1]A. Fry, "Stickstoff in Eisen, Stahl und Sonderstahl." *Stahl und Eisen*, Vol. 43, 1923, p. 1271. *Kruppsche Monatshefte*, Vol. 4, 1923, p. 138.

*Publication approved by the director of the Bureau of Standards of the U. S. Department of Commerce.

The author, who is a member of the society, was formerly with the metallurgical division of the Bureau of Standards at Washington, but is now associated with the Illinois Steel Company of South Chicago. Manuscript received June 10, 1929.

degrees Cent. (930-1020 degrees Fahr.) and much less soluble at room temperature. This suggested to Griffiths[2] that nitrogen may be a factor in the temper brittleness of steel and he obtained evidence tending to support this view. More recently, Dean, Day, and Gregg[3] showed, as was predicted by Sawyer[4] that the needle-like iron nitride constituent causes precipitation or dispersion hardening in iron and therefore likewise suggested that temper brittleness and blue heat phenomena in iron may be due to nitrogen.

The accurate determination of the iron-nitrogen diagram, especially for alloys of high nitrogen content, is extremely difficult. Fairly homogeneous alloys of iron and nitrogen of very low nitrogen content can be obtained by melting iron in an atmosphere of nitrogen but alloys of high nitrogen content cannot be produced in this way, even under very high pressures of nitrogen. Under a pressure of 3 atmospheres Sawyer[5] obtained an alloy of 0.034 per cent[6] nitrogen content, under 200 atmospheres Andrew[7] obtained an alloy of 0.3 per cent nitrogen, and according to a calculation by Sawyer, under 900 atmospheres an alloy of 0.6 per cent should be obtained. According to Sawyer's calculation, the constant, 0.02, multiplied by the square root of the nitrogen pressure gives the per cent of nitrogen in the alloy. Since the nitrogen pressure enters into this formula as the square root it will be apparent, if the formula is even approximately correct, that obtaining very high nitrogen content in iron by melting under pressure is hardly practicable.

The usual method of introducing nitrogen into iron is by diffusion into hot solid iron; molecular nitrogen does not diffuse appreciably, and nascent nitrogen, such as is formed in "cracking" am-

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[2]W. T. Griffiths: Note on Nitrogen as Possible Factor in Temper Brittleness. *Journal*, Iron & Steel Institute, Vol. 111, No. 1, 1925, p. 257.

[3]R. S. Dean, R. O. Day, J. L. Gregg: Relation of Nitrogen to Blue Heat Phenomena in Iron and Dispersion Hardening in the System Iron-Nitrogen. Technical Publication No. 193, A. I. M. E., 1929.

[4]C. B. Sawyer: Nitrogen in Steel: *Transactions*, American Institute Mining and Metallurgical Engineers, Vol. 49, 1923, p. 799. The Reactions and Effects of Nitrogen in Steel. TRANSACTIONS, American Society for Steel Treating, Vol. 8, 1925, p. 291.

[5]C. B. Sawyer: Nitrogen in Steel, *Transactions*, A. I. M. E., Vol. 49, 1923, p. 799.

[6]All percentage figures for nitrogen used herein are by weight, not by volume. The nitrogen determinations of the specimens used in this investigation were made by L. Jordan and associates.

[7]J. H. Andrew: The Influence of Gases Upon the Critical Ranges of the Iron-Carbon Alloys—Iron and Steel Institute, Carnegie Scholarship Memoirs III, 1911, p. 236.
Iron and Nitrogen, *Journal*, Iron and Steel Institute, Vol. 86, 1912, p. 210.

monia gas by passing it over hot iron, is necessary. In this way iron-nitrogen alloys containing a maximum of about 11 per cent nitrogen may be produced. However, the nitriding is not uniform but takes place by the formation of several distinct layers of different iron-nitrogen compounds and constituents, so that the chemical composition of even a very small nitrided particle may vary discontinuously from a small fraction of a per cent near the center to the maximum of about 11 per cent nitrogen at the surface. The difficulty of determining and interpreting critical points in such specimens by a precise method such as thermal analysis is manifest. Moreover, there is the added difficulty that the nitride layers are very unstable, nitrogen gas being liberated upon heating to temperatures as low as 300 degrees Cent. (570 degrees Fahr.) and the gas evolution increasing rapidly at higher temperatures. Thus, during a thermal analysis, the chemical composition of the specimen is always changing, and the heat effects produced by the gas evolution may obscure transformation points or be mistaken for them. The fact that the iron-nitrogen alloys decompose when heated makes it practically impossible to obtain homogeneous specimens by annealing, except those of comparatively low nitrogen content. The determination of the iron-nitrogen diagram by the use of nitrided specimens may be likened to a hypothetical study of the iron-carbon diagram in which only carburized specimens were available, wherein not only one iron-carbide was formed but two or more, and in which the carbon escaped continually on heating and cooling.

Early in 1922, before either Sawyer's or Fry's work was published, the Bureau of Standards began a series of thermal analyses of nitrided specimens. While it soon became evident that thermal analysis alone is insufficient for establishing the relationships between iron and nitrogen, the work was continued as time permitted. Within the last year, however, the work has been more active and an attempt has been made, with the diagrams of Sawyer and Fry as a basis, and with the help of the thermal analysis data, supplemented by microscopic and X-ray examinations, to re-survey some portions of the iron-nitrogen system.

No claim whatever is made that the present paper completely settles the iron-nitrogen constitution diagram. Some of the interpretations of the data are matters of opinion. In a system beset with so many difficulties, final conclusions cannot be hastily drawn.

II. Discussion of Sawyer's and Fry's Diagrams

A brief discussion may here be given of the two existing diagrams of the iron-nitrogen system determined independently by Sawyer[8] and by Fry[9] at about the same time, in 1923. These diagrams are shown in Figs. 1 and 2. Sawyer depended largely on

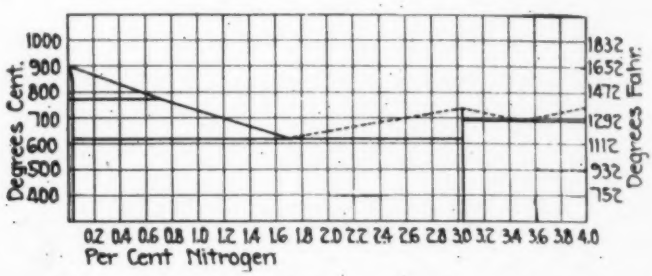

Fig. 1—Sawyer's Iron-Nitrogen Constitution Diagram.

thermal analysis, which he supplemented by microscopic examinations. Fry, on the other hand, in view of the previously mentioned difficulties involved in thermal analysis, avoided this method entirely and relied mainly on microscopic examinations. Fry worked with a 0.1 per cent carbon steel and Sawyer with very low carbon sheet iron.

On the lower nitrogen side of the diagram Sawyer and Fry are in substantial agreement. The diagram in this region closely resembles the iron-carbon diagram. Nitrogen, like carbon, lowers the A_3 point of iron and a eutectoid, Braunite, a constituent named for one of the first investigators[10] to study this system, occurs similar to pearlite in steel but contains about twice as much nitrogen as the carbon content in pearlite. Sawyer placed the nitrogen content of Braunite at 1.7 per cent, Fry at 1.5 per cent. The eutectoid horizontal in the iron-nitrogen system is about 100 degrees Cent. lower than in the iron-carbon system. Sawyer placed it at 620 degrees Cent. (1150 degrees Fahr.) and Fry at 580 degrees Cent. (1075 degrees Fahr.) The solid solubility of nitrogen in iron at room temperature is quite low, Sawyer, placed it at 0.03 per cent and Fry at 0.015 per cent. This is somewhat higher than the solubility of carbon in iron

[8]C. B. Sawyer, see footnote 5.

[9]A. Fry, see footnote 1.

[10]H. Braune: Influence De L'Azote Sur Fer et L'Acier. *Rev. de Metallurgie*, Vol. 2, 1905, p. 498; Vol. 4, 1907, p. 834 *Stahl und Eisen*, Ueber die Bedeutung des Stickstoffes im Eisen, Vol. 26, 1906, p. 1357.

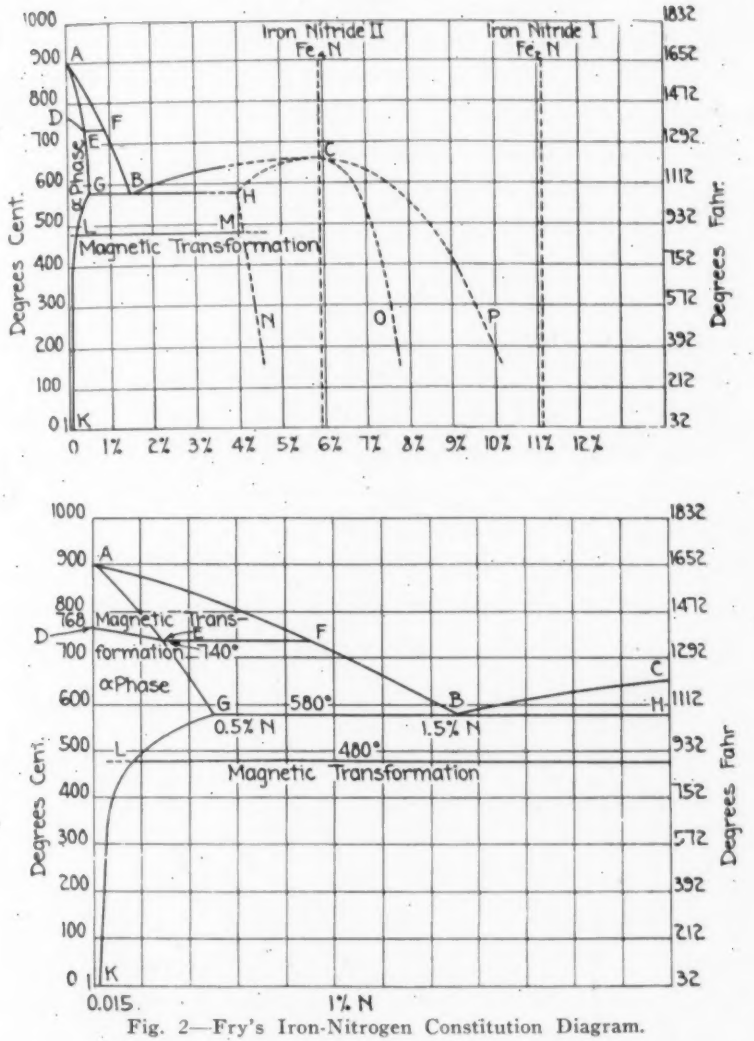

Fig. 2—Fry's Iron-Nitrogen Constitution Diagram.

at room temperature which is considered to be below 0.01 per cent[11]. Sawyer did not determine the solubility of nitrogen at the eutectoid horizontal, but Fry sets this at the very appreciable value of 0.5 per cent; in this respect there is considerable difference between the behavior of carbon and nitrogen, since the solubility of the former at the A_1 point is not very much higher than at room temperature, it being generally placed at about 0.035 per cent.

For alloys of higher nitrogen content Sawyer's and Fry's diagrams are at considerable variance, as may be briefly pointed out. Sawyer considered the nitrogen compound which, together with iron, forms the eutectoid, Braunite, to be Fe_8N whereas Fry considers it

[11] H. W. Gillett: Discussion of paper by M. A. Grossmann, "On Oxygen Dissolved in Steel, and Its Influence on the Structure," presented at A. S. S. T. Convention, 1928.

to be Fe_4N. Sawyer, from his thermal analyses and from microscopic evidence which will be discussed later, decided that there was another eutectoid transformation, which takes place at 690 degrees Cent. (1275 degrees Fahr.) between the compounds Fe_8N and Fe_6N. Fry's diagram does not contain this horizontal. Sawyer did not continue his diagram beyond the compound Fe_6N (4 per cent nitrogen) but Fry also included the compound Fe_2N (11.3 per cent nitrogen) which he indicated to be unstable.

Fry also made magnetic measurements and placed a magnetic transformation horizontal across the lower nitrogen side of the diagram at 480 degrees Cent. (895 degrees Fahr.) Indications of thermal transformations, in the form of "swings" instead of definite arrests, in this temperature range were obtained in the Bureau's thermal analyses, but it is not certain that the magnetic transformation had any relationship to the low temperature "swings." It may be stated here that the interpretation of these thermal effects was not sufficiently clear to warrant representing them by lines on the constitution diagram.

Before entering into an examination of the evidence on which the above diagrams are based, the data obtained in the Bureau's work on the subject will be presented.

III. Thermal Analyses[12]

To obtain as uniform distribution of nitrogen as possible Sawyer nitrided thin disks of sheet iron 0.228 millimeters thick which he piled on top of one another to form his thermal analysis specimens. At the Bureau, after some preliminary work with solid pieces of iron, it was decided to use electrolytic iron crushed, before nitriding, into granules to pass through a 20-mesh sieve and in later work through a 30-mesh sieve. The nitrided granules were at first packed in a small alundum crucible around the thermocouple bead but later they were briquetted under 75,000 pounds per square inch pressure in a steel die. The briquetted granules, except those of the highest nitrogen content, could then be handled in the same way as the ordinary solid specimen.

For nitriding, very pure ammonia gas obtained from the Fixed Nitrogen Research Laboratory was used; this was purified by passing through soda lime and solid caustic potash. After nitriding,

[12]This section is based on thermal analyses carried out by Miss I. J. Wymore and H. C. Cross.

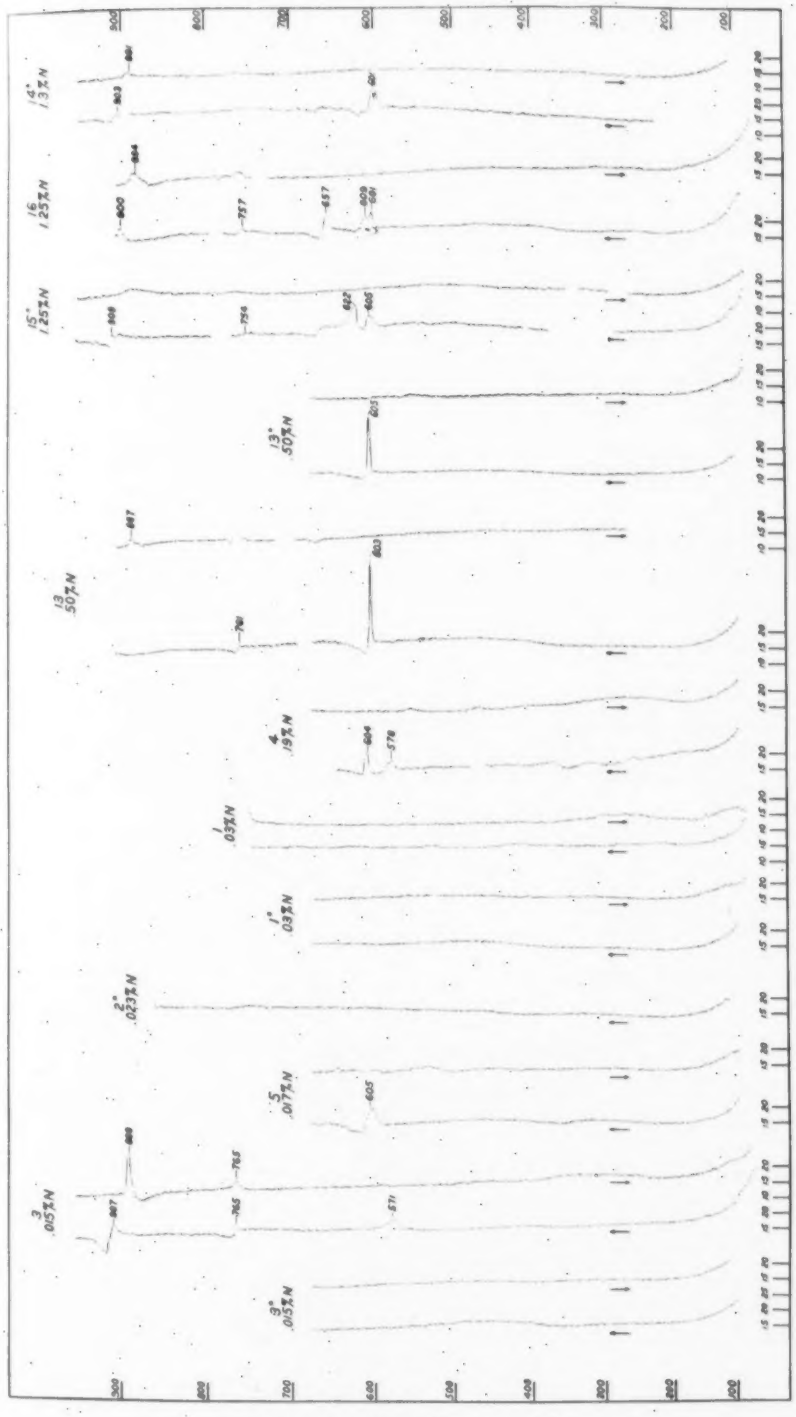

Fig. 3—Thermal Analysis Curves of Nitrided Electrolytic Iron Granules.

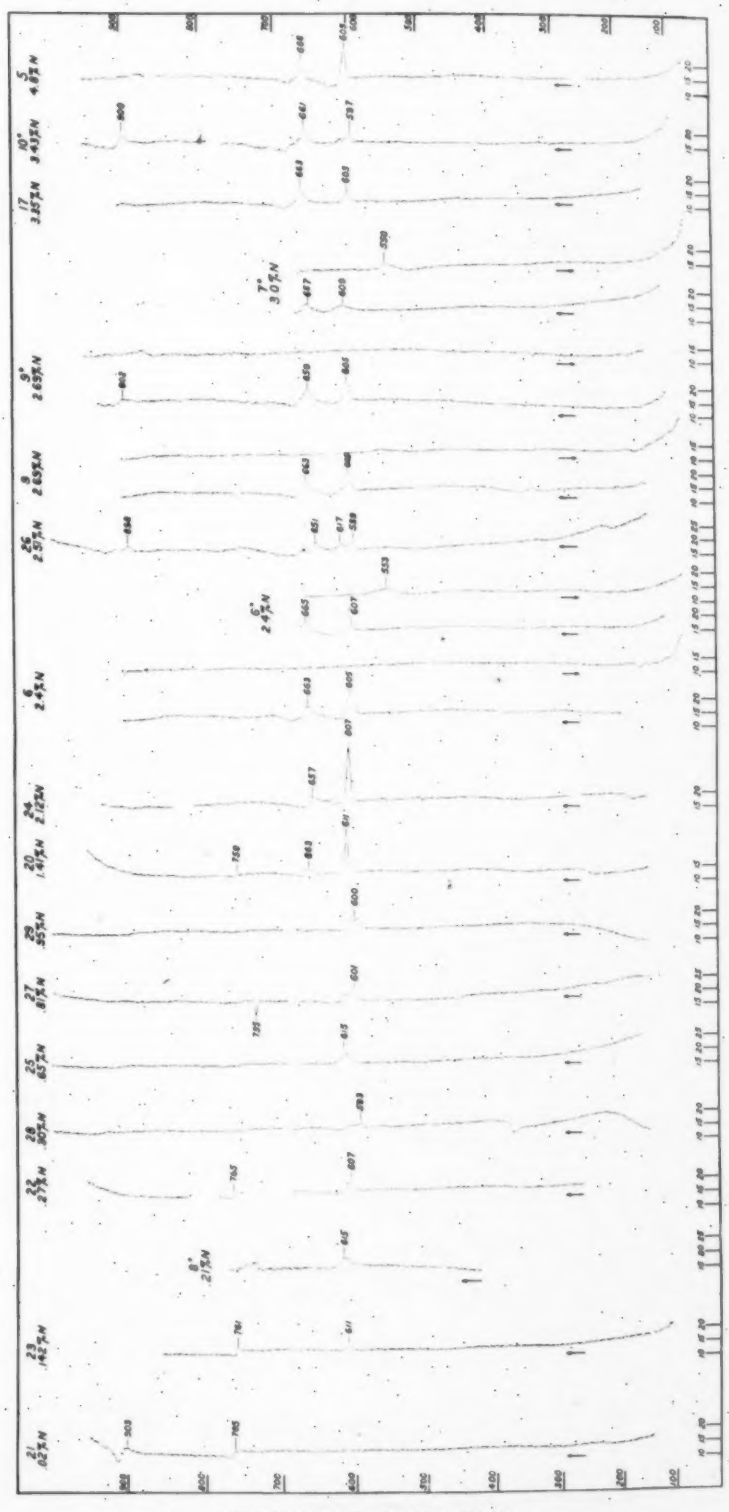

Fig. 4—Thermal Analysis Curves of Nitrided Electrolytic Iron Granules.

some of the specimens were annealed in nitrogen in an effort to make them more uniform in composition. However, despite all precautions uniform specimens were not obtained, so that the thermal analysis results lack the precision which is usually associated with this method, and throw light on only a very restricted field of the iron-nitrogen system.

The inverse rate thermal analysis apparatus and methods used at the Bureau of Standards are described by Scott and Freeman[13], and by French[14].

The results of the thermal analyses are shown in Figs. 3 and 4 and are summarized in Fig. 5. A detailed analysis of the results need not be made here[15] and it will be sufficient to point out that, as

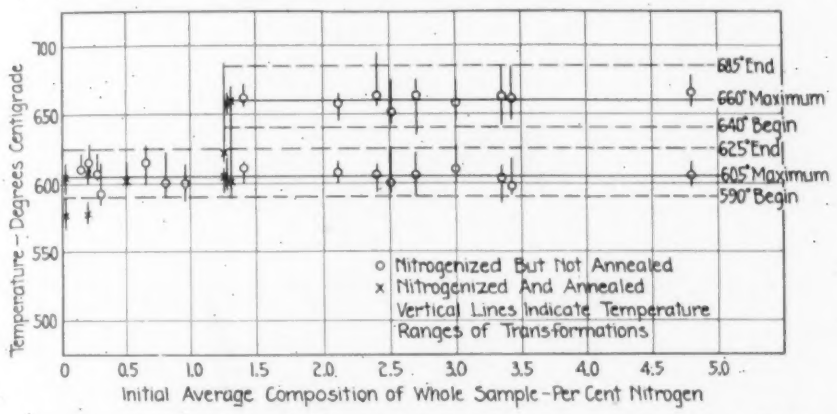

Fig. 5—Summary of Thermal Analysis Curves. The points indicate arrests on the inverse rate heating curves.

shown in Fig. 5, Sawyer's two arrests in the higher nitrogen alloys were confirmed. The lower one, which undoubtedly represents the Braunite eutectoid transformation, may be set from these results at 605 degrees Cent. (1120 degrees Fahr.) The upper horizontal which occurred only in alloys of average composition 1.25 per cent nitrogen or higher may be set at 660 degrees Cent. (1220 degrees Fahr.) It may be stated here that microscopic examination indicated that this upper transformation could not be due to another eutectoid on the higher side of the diagram as Sawyer decided, but that it was probably due to a peritectoid reaction above the eutectoid horizontal.

[13]H. Scott, J. R. Freeman: Use of a Modified Rosenhain Furnace for Thermal Analysis, Bureau of Standards Scientific Paper 348, 1919.

[14]H. J. French: A Recording Chronograph for the Inverse Rate Method of Thermal Analysis, Bureau of Standards Technologic Paper 230, 1923.

[15]A fuller analysis of the results and a detailed description of the method of preparation and average nitrogen content of the specimens which were used will be given in a forthcoming Bureau of Standards Research Paper on this subject.

Another point on which the thermal analyses throw some light is the solid solubility of nitrogen in iron. In a specimen containing 0.2 per cent average nitrogen (see curve of spec. 4, Fig. 3) the arrest in the eutectoid transformation range was not sharp, as in a specimen containing 0.5 per cent average nitrogen (see curves of spec. 13, Fig. 3), but doubled. A possible interpretation of this is that the lower portion of the double transformation represents the solution of the nitride in α iron and the upper portion the eutectoid transformation of that zone of the specimen having a higher nitrogen content. If this view is correct, it would indicate appreciable solubility of nitrogen in iron at the eutectoid transformation temperature, and thus partly substantiate Fry's figure of 0.5 per cent. That a definite arrest was obtained in the specimen of 0.5 per cent average nitrogen content cannot be considered as evidence that no more than this content is soluble, because of the lack of uniformity in the composition of the specimens. In this range the average nitrogen content appears to be roughly only about a third of that of the outer layer. For the same reason, the thermal analyses of the specimens in the range between 0.2 per cent and 0.5 per cent average nitrogen give no definite evidence on the matter; some show a fairly sharp arrest and others a rounded or doubled transformation (see curves of specimens 23, 8, 22, and 28, Fig. 4). The indications of thermal effects or "swings" in the curves in the temperature range 300-450 degrees Cent. (570-840 degrees Fahr.) which have been mentioned, may be noticed for many of the specimens of Figs. 3 and 4. The "swings" were so indefinite that no positive interpretation of these effects seemed justified.

IV. Microscopic Examination

In examining under the microscope, cross-sections of the granules used in the thermal analyses, the two layers described by Fry as Nitride I and Nitride II and considered by him to be solid solutions of the compounds Fe_2N and Fe_4N, respectively, were recognized. However, no eutectoid between the two layers was found such as Sawyer reported. His explanation that the upper horizontal shown by thermal analysis represented a eutectoid transformation can only hold if such a eutectoid exists. The other possible way of accounting for the upper horizontal, namely, that it represents a peritectoid reaction is, therefore, suggested. This, however, calls for the presence of another compound, as will be seen from the construction of this

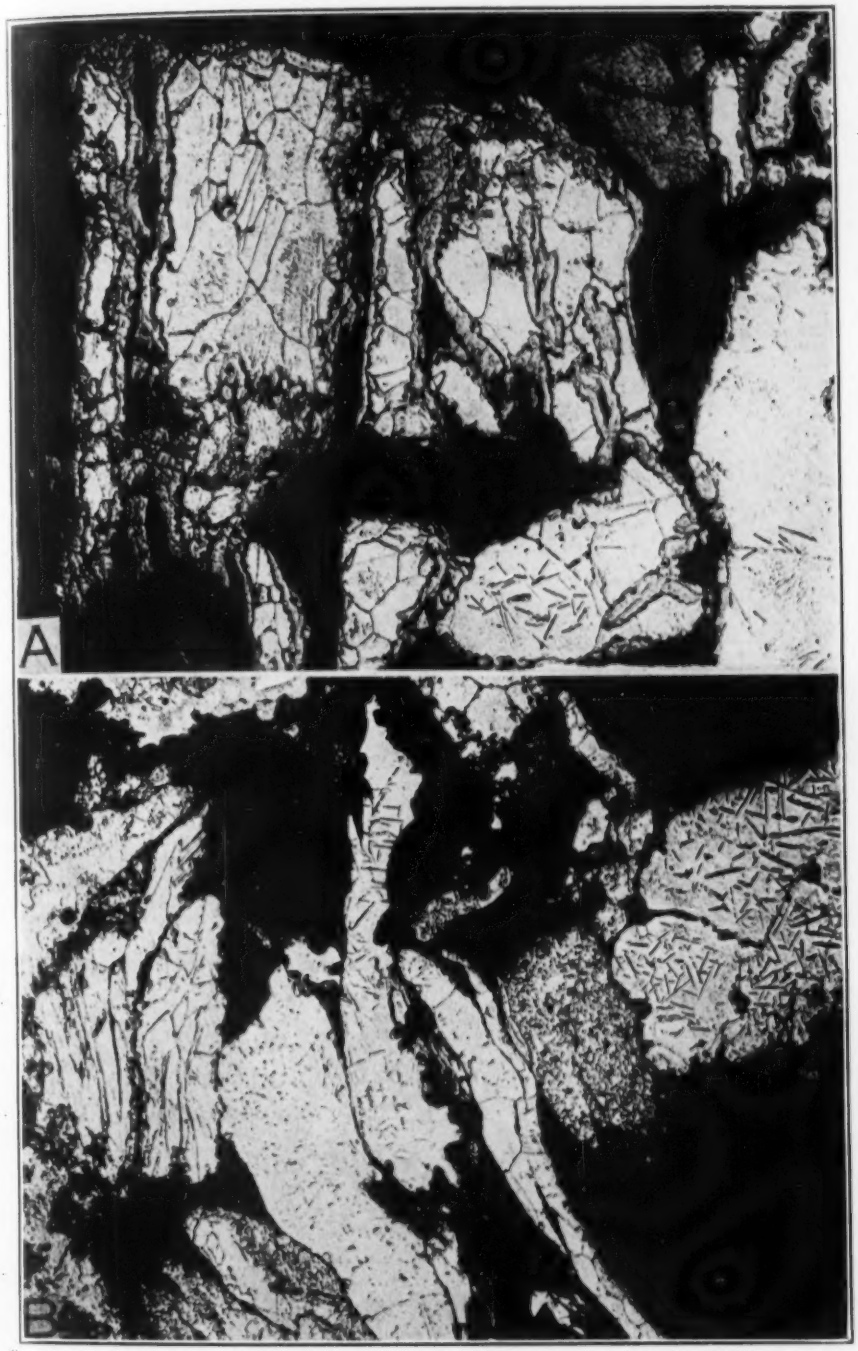

Fig. 6—Non-Uniform Penetration of Nitrogen in Nitrided Electrolytic Iron Granules Used for Thermal Analyses, × 100. All specimens etched with 5 per cent picric acid unless otherwise stated.

A. Spec. No. 7 nitrided at 550 degrees Cent. (1020 degrees Fahr.) for 2 hours; average nitrogen content 3 per cent. The bulk of the nitrogen in this specimen was concentrated in the thin surface layers.

B. Spec. No. 13 nitrided at 650 degrees Cent. (1200 degrees Fahr.) for ½ hour; average nitrogen content 0.5 per cent.

Fig. 7—What Appear to be Nitride Needles in a Specimen Very Low in Nitrogen, × 500.
Spec. 5a nitrided at 950 degrees Cent. (1740 degrees Fahr.) for 1 hour then annealed at 950 degrees Cent. in nitrogen for 1 hour; average nitrogen content 0.01 per cent.

type of diagram as shown in Fig. 20. Meanwhile, in examining blocks of remelted electrolytic iron specially nitrided for the purposes of microscopic examination, an extreme outer layer not hitherto observed in the granules and not described by Fry, was detected. At first, this surface layer was thought to be due to oxide resulting from moisture in the ammonia gas used, but when the layer still appeared after the ammonia was dried with metallic sodium, it was decided to be another nitride layer. The support this gave to the supposition that the upper horizontal represented a peritectoid reaction, was recognized, and the regions in the diagram on both sides of this line were explored by microscopic examination for further confirmation. This, it appears, has been obtained.

The details of the microscopic examination will now be described. Fig. 6 shows the appearance of sections through the granules of two thermal analysis specimens. The structures shown are representative, in regard to uniformity and depth of nitriding, of all the thermal analysis specimens. As may be seen, the nitrogen pene-

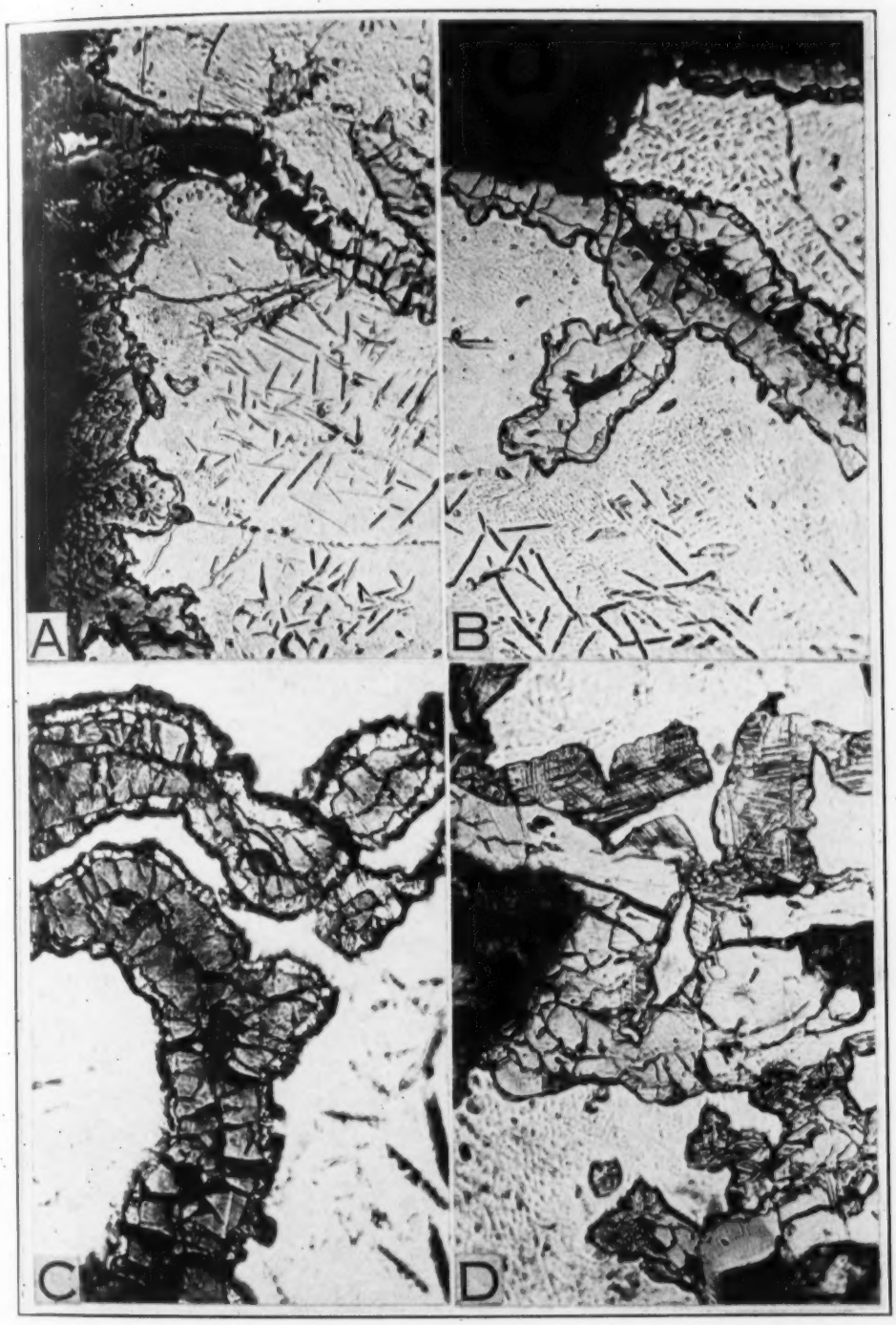

Fig. 8—Layers in Nitrided Electrolytic Iron Granules.

A. Spec. No. 7 nitrided at 550 degrees Cent. (1020 degrees Fahr.) for 2 hours; there is a fairly thick outer layer and a thin ribbon of an inner layer can be distinguished, × 250.

B. Same as A, × 500.

C. The same specimen more deeply etched. Taken along crevice which the nitrogen penetrated. The "inner layer" is adjacent to the electrolytic iron. The "outer layer" extends on both sides of the crevice. Even after the rather prolonged etching the outer layer remained unattacked. In the inner layer what appears to be a twinned structure can be distinguished, × 500.

D. Spec. No. 10, nitrided at 550 degrees Cent. (1020 degrees Fahr.) for 5 hours. The outer layer has smooth appearance; it is not attacked by the etching solution. The inner layer is covered with a series of slip lines.

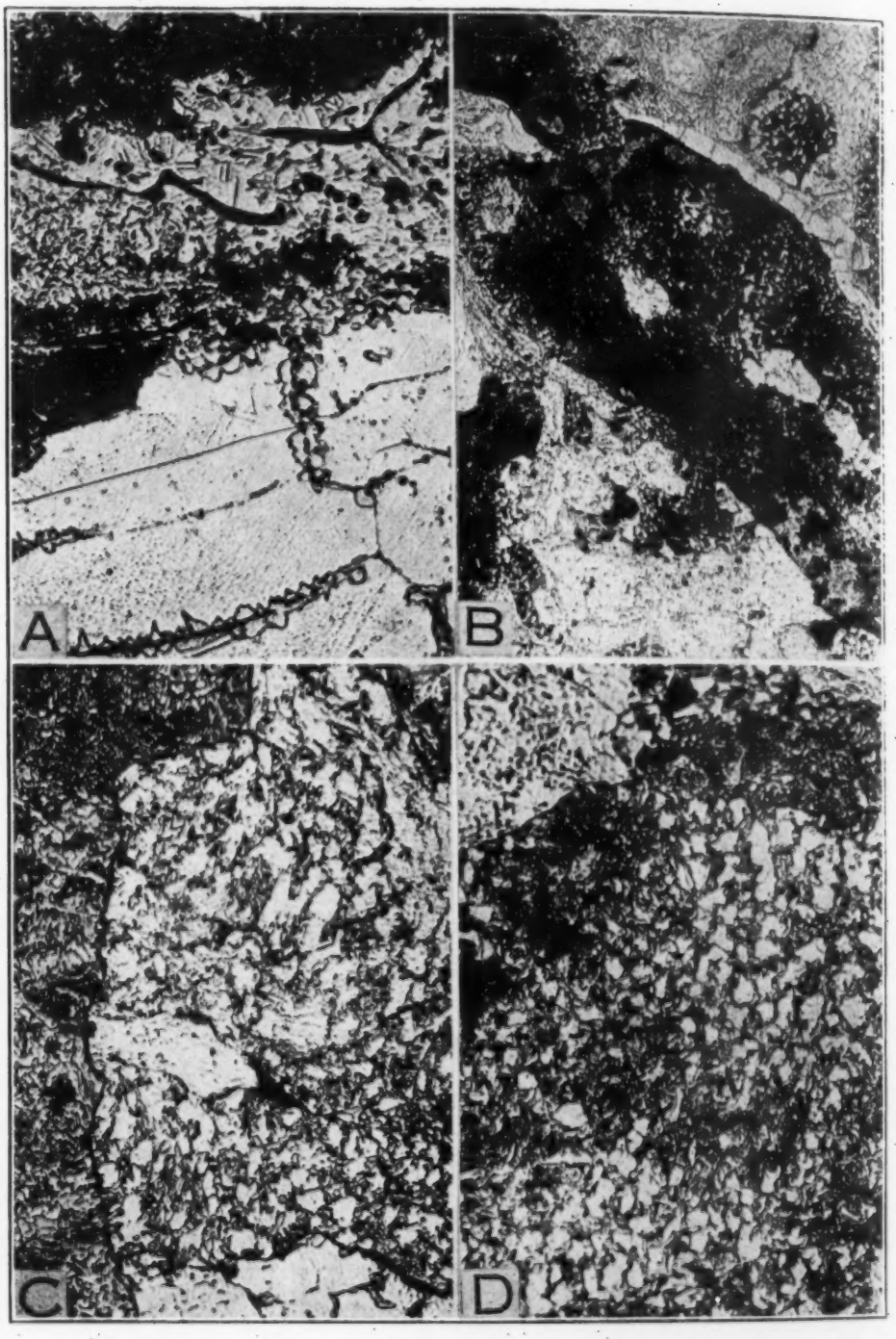

Fig. 9—The Eutectoid Braunite Containing About 1.5 per cent Nitrogen.

A. Spec. No. 6 nitrided at 650 degrees Cent. (1200 degrees Fahr.) for 1 hour; average nitrogen content 2.4 per cent, × 500. The background is the core of electrolytic iron. The dark constituent is the eutectoid Braunite. The white constituent, is the "inner layer."

B. Spec. No. 10 nitrided at 550 degrees Cent. (1020 degrees Fahr.) for 5 hours and then annealed at 685 degrees Cent. (1265 degrees Fahr.) in vacuum, average nitrogen content 0.49 per cent, × 100.

C. Same as B, × 500.

D. Spec. No. 9 nitrided at 650 degrees Cent. (1200 degrees Fahr.) then annealed at 685 degrees Cent. (1265 degrees Fahr.) in vacuum. The dark constituent is Braunite.

tration was not uniform, most of it being concentrated in the surface layers.

Fig. 7 shows the structure of a specimen, which on chemical analysis was found to contain only 0.01 per cent average nitrogen. The presence of what appear to be nitride needles is of interest, for it may indicate that the solid solubility of nitrogen in iron may be even lower than the value, 0.015 per cent, given by Fry. It should be remembered, however, that too great reliance cannot be placed in the values obtained for nitrogen content due to lack of homogeneity of the specimens.

The layers designated in Fry's micrographs as Nitride I and Nitride II may be seen in Fig. 8, the thicker outer layer being Nitride I and the thinner inner layer Nitride II. The outer layer is light brown in color and is not appreciably attacked by 5 per cent alcoholic picric acid. The thin inner layer is a lighter cream color, is attacked by picric acid, and also is colored dark brown by boiling sodium picrate; it exhibits twinning as was noted by Fry and Sawyer. A characteristic of this inner layer, which apparently has not been previously noted, is its tendency to form slip lines as shown. These probably arose when the granules were compressed into the briquettes used for thermal analysis; that the inner layer is particularly prone to form slip lines is evident from the absence of these lines in the adjacent outer layer and in the electrolytic iron in the interior. It appeared evident from the etching characteristics of the nitride needles that, as has also been noted by Fry, they are composed of the same constituent as the inner layer.

In the specimens nitrided below 600 degrees Cent. (1111 degrees Fahr.) only the above mentioned layers and the nitride needles were present. In those nitrided above 600 degrees Cent. (1111 degrees Fahr.), however, the eutectoid, Braunite, also appeared. This is the dark constituent, resembling pearlite, shown in Fig. 9. It always appeared on the interior side of Nitride II; without doubt. Braunite is a eutectoid of this compound and iron. Fig. 9b depicts a nitrided specimen annealed in vacuum at 685 degrees Cent. (1265 degrees Fahr.), after which it contained 0.5 per cent average nitrogen. As shown in the micrograph, the specimen was composed of approximately 1/3 eutectoid and this, therefore, roughly confirms Sawyer's and Fry's values for the eutectoid composition of 1.5 per cent nitrogen.

Thus far only the structures of the electrolytic iron granules

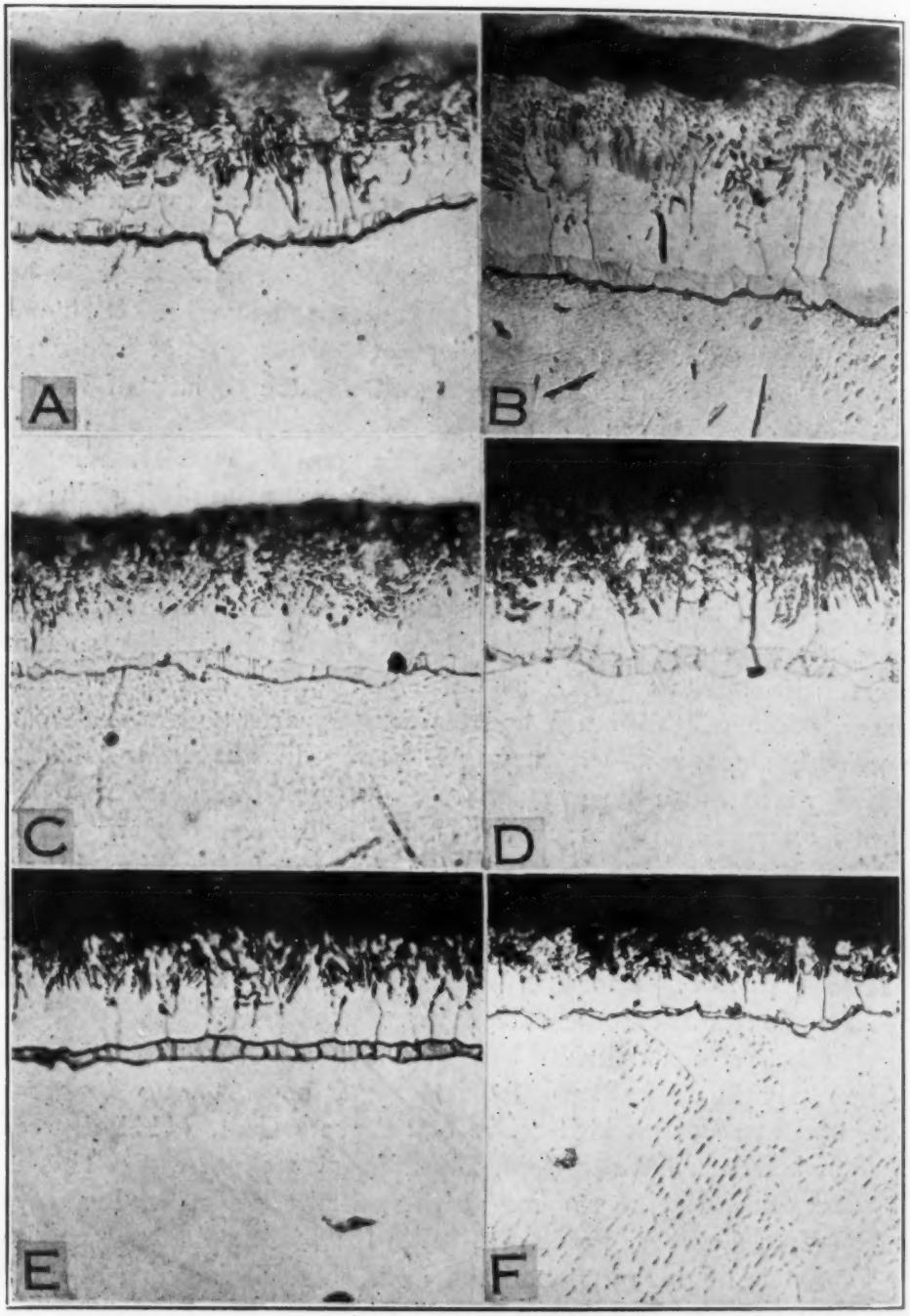

Fig. 10—Appearance of Nitrided Layers in Remelted Electrolytic Iron Blocks, × 500.
Three distinct nitride layers can be distinguished. The extreme outer layer has previously not been noted. The nitriding temperatures of the specimens which showed a well defined extreme outer layer were rather low; 550 degrees Cent. (1020 degrees Fahr.) or lower.

A. Nitrided 75 hours at 500 degrees Cent. (930 degrees Fahr.)
B. Nitrided 25 hours at 550 degrees Cent. (1020 degrees Fahr.)
C. Nitrided 25 hours at 550 degrees Cent. (1020 degrees Fahr.)
D. Nitrided 75 hours at 500 degrees Cent. (930 degrees Fahr.) etched in alkaline sodium picrate.
E. Nitrided 25 hours at 550 degrees Cent. (1020 degrees Fahr.); etched in alkaline sodium picrate.
F. Nitrided 170 hours at 425 degrees Cent. (795 degrees Fahr.)

Boiling alkaline sodium picrate etches the inner layer brown or dark brown depending on the length of etching. The extreme outer layer has the appearance of a eutectoid and is etched by both picric acid and sodium picrate.

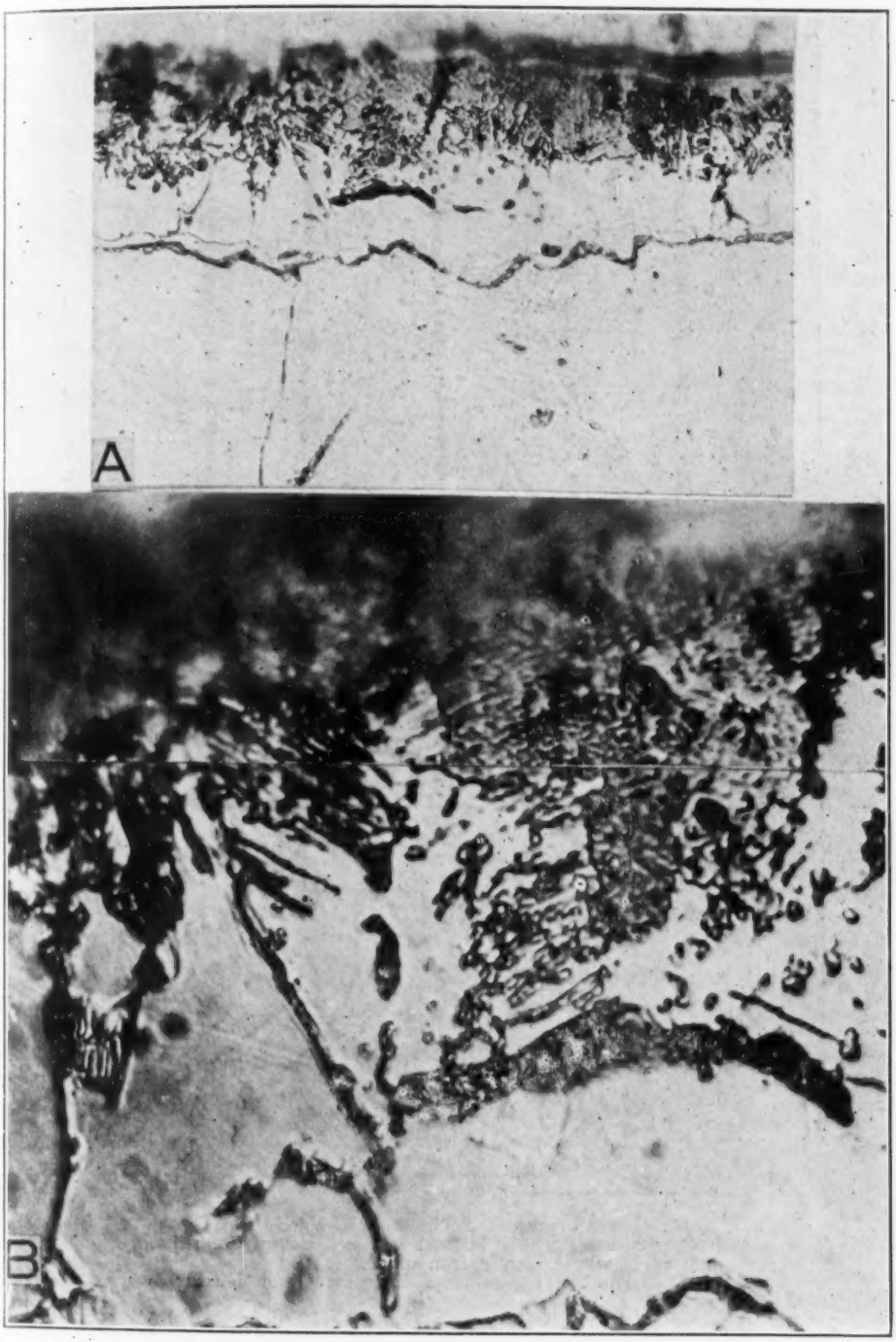

Fig. 11—Appearance of Extreme Outer Layer of Nitrided Iron Block.
A. Nitrided 75 hours at 500 degrees Cent. (930 degrees Fahr.) × 500.
B. Same spot, × 2000.

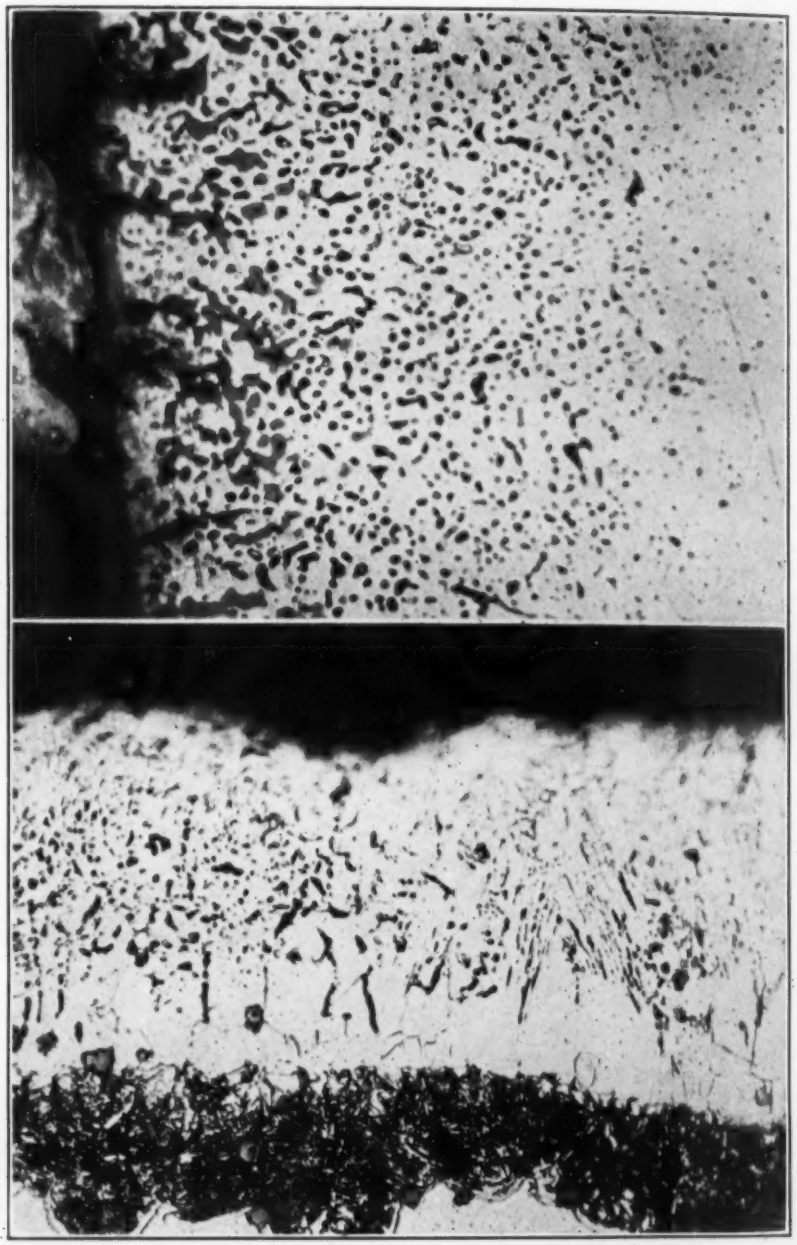

Fig. 12—Oxide constituent at Surface of Nitrided Iron Block, × 500. The edge of the specimen is at the left side. The dark gray constituent lining the cracks and voids was evidently iron oxide.

Fig. 13—Apparent Decomposition of Extreme Outer Nitride Layer, × 500.

Nitrided 25 hours at 600 degrees Cent. (1110 degrees Fahr.). The voids and fissures in the extreme outer layer indicate the decomposition of the outermost constituent.

used for thermal analysis have been considered. Since it was difficult to prepare these granules satisfactorily for microscopic exami-

nation, small blocks of remelted electrolytic iron were nitrided and used. These were mounted in solder before polishing so that the sections could be observed to the extreme edge. The specimens were not ground on an abrasive wheel, but were smoothed down on emery paper laid on a board, this precaution being taken in order not to risk breaking off any of the nitrided layers.

In these nitrided blocks an extreme outer layer not described by Fry, lying outside the layer designated in his micrographs as Nitride I, was detected. The appearance of this layer, which has a eutectoid structure, is shown in Figs. 10 and 11 (in these and subsequent figures the outer nitride layer is at the top or at the left of the micrographs). In examining nitrided electrolytic iron specimens received from another laboratory, the outside layer was observed and found to contain an oxide constituent as shown in Fig. 12. However, that the whole outer layer was not due to oxide appeared evident because, as previously mentioned, specimens nitrided in ammonia completely freed from moisture by the use of metallic sodium still showed the outer layer. This layer in the unetched state resembles that of iron oxide, although the layer is considerably lighter and can readily be distinguished from iron oxide. After etching with either picric acid or sodium picrate the appearance of the outer layer may be even more readily distinguished from that of iron oxide similarly etched.

The extreme outer layer just described was not noted by Fry, due perhaps to the rounding and cracking of the edges of his polished sections, but more probably because at the high temperature 680 degrees Cent. (1255 degrees Fahr.) at which the specimens shown in his micrographs were nitrided, the outer constituent is decomposed and only voids and fissures remain in its place. This is shown in some of Fry's micrographs but he did not discuss this feature of the structure. The "decomposed appearance" of the structure of the outer layer upon nitriding at 600 degrees Cent. (1111 degrees Fahr.) or higher is shown in Fig. 13 and in the other figures of similar specimens.

Because the newly found layer has a eutectoid structure, the question may arise whether it is not the eutectoid which Sawyer considered to be formed at the upper horizontal. The evidence indicates very strongly, however, that this layer is not the eutectoid in question. The layer is at the extreme outside and cannot, therefore, be a eutectoid between the two inner nitride compounds as indicated

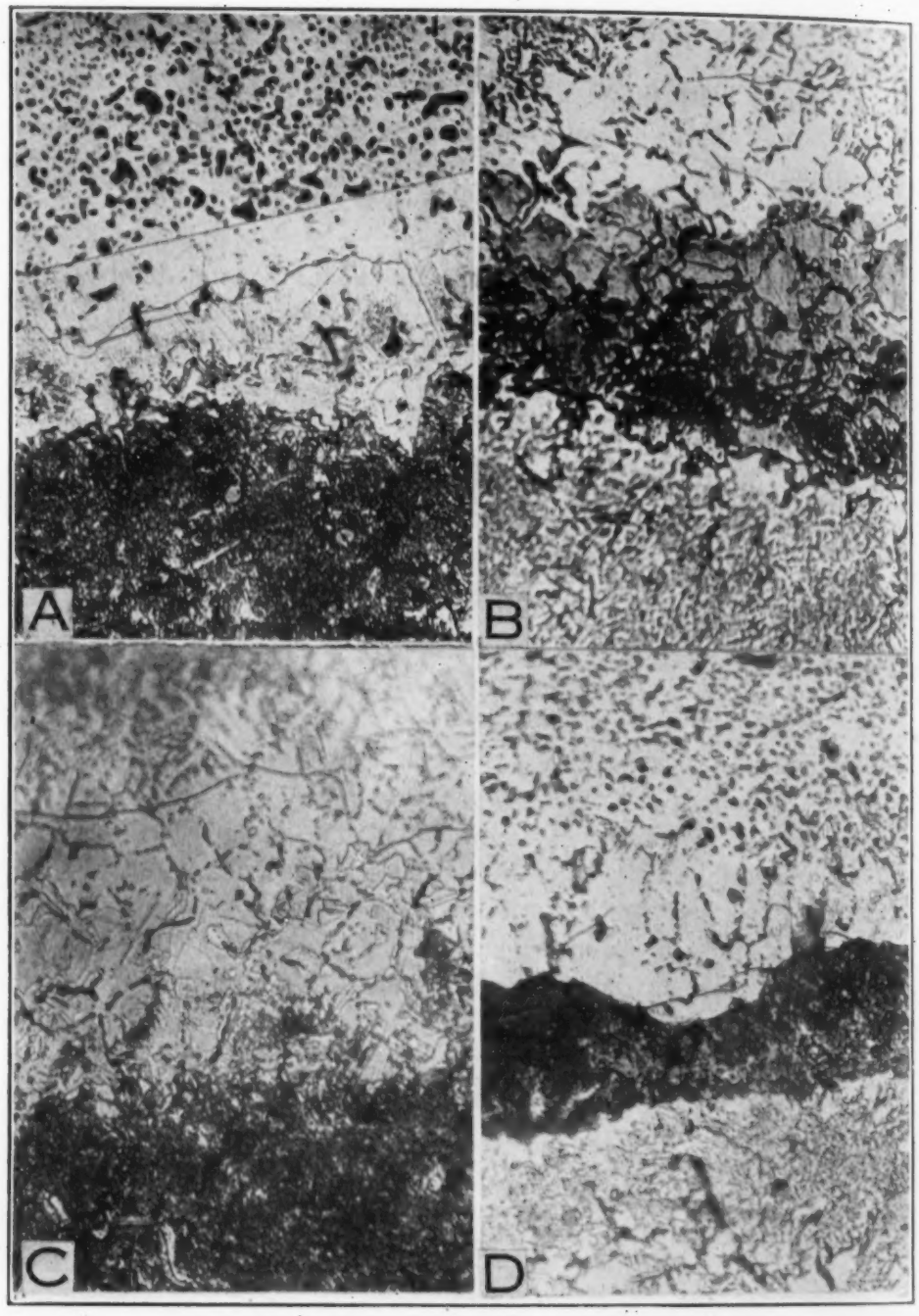

Fig. 14—Appearance of Nitrided Iron Blocks Heated above Upper Horizontal and Slowly Cooled, × 500.

A. Nitrided 25 hours at 600 degrees Cent. (1110 degrees Fahr.) then heated ½ hour in NH_3 at 685 degrees Cent. ((1265 degrees Fahr.) and furnace cooled.

B. Same as A, etched with sodium picrate.

C. Nitrided 75 hours at 500 degrees Cent. (930 degrees Fahr.) then heated ½ hour in NH_3 at 685 degrees Cent. (1265 degrees Fahr.) and furnace cooled.

D. Same as C, etched with sodium picrate.

At the bottom of each micrograph the eutectoid Braunite is shown; this etches darker with picric acid than with sodium picrate; the inner nitride layer is etched a dark brown by the latter reagent.

No signs of the formation of a eutectoid between the two inner nitride layers can be detected.

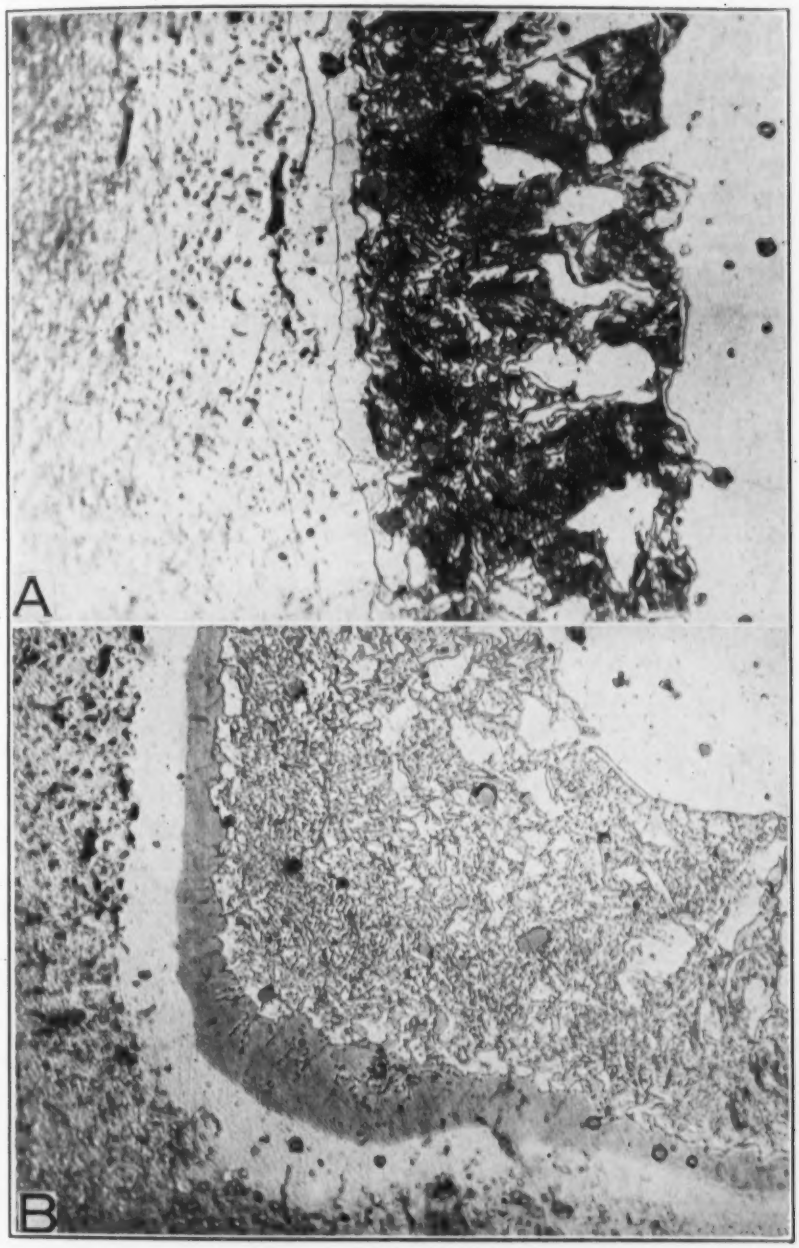

Fig. 15—Appearance of Nitrided Iron Blocks Heated above Upper Horizontal and Slowly Cooled, × 500.

A. Nitrided 50 hours at 500 degrees Cent. (930 degrees Fahr.) then heated ½ hour in NH_3 at 725 degrees Cent. (1335 degrees Fahr.) and furnace cooled. The edge of the specimen is at the left.

B. Nitrided 25 hours at 600 degrees Cent. (1110 degrees Fahr.) then heated ½ hour in NH_3 at 725 degrees Cent. (1335 degrees Fahr.) and furnace cooled; etched with sodium picrate.

It is quite plain that no eutectoid was formed between the two inner nitrided layers.

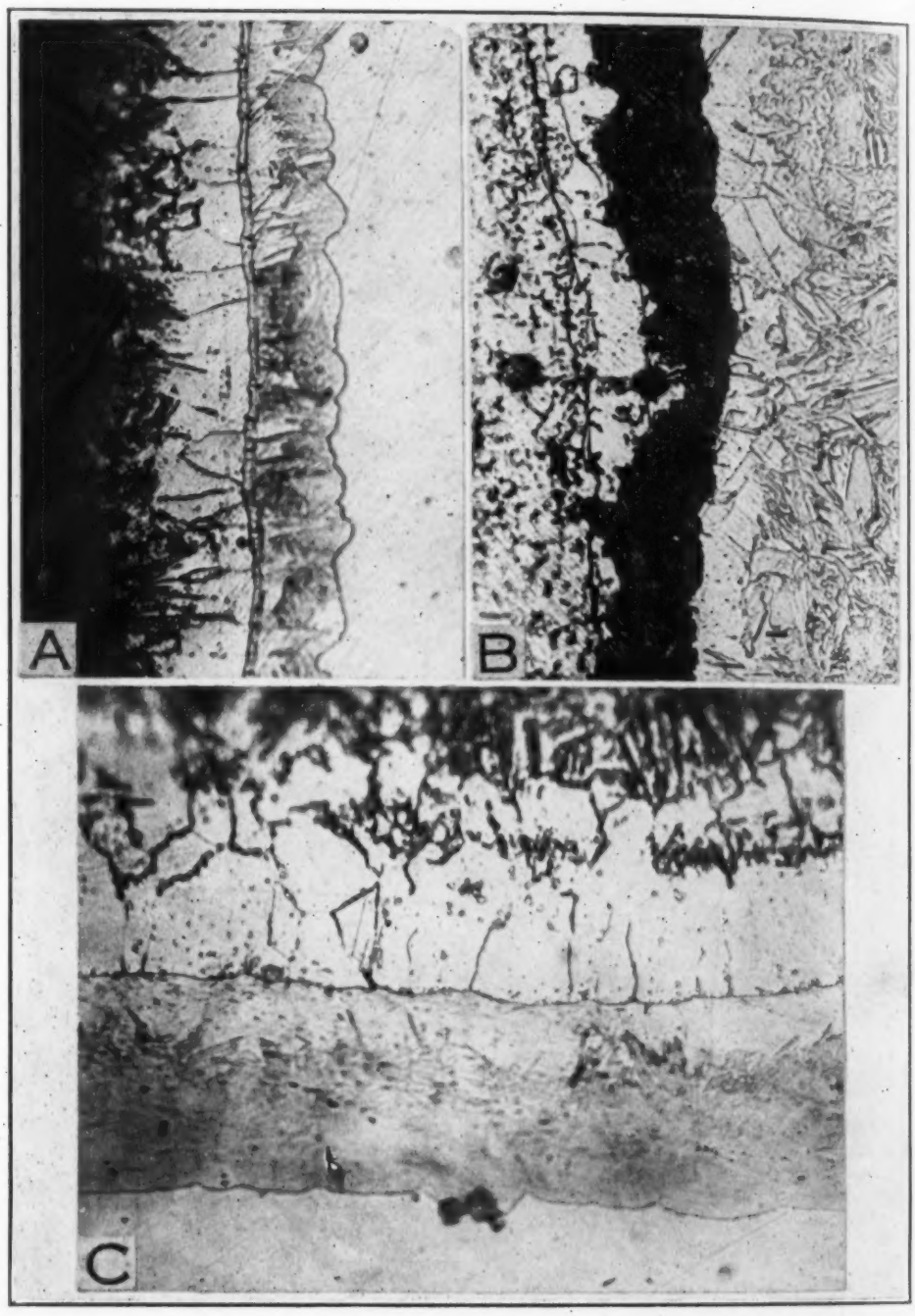

Fig. 16—Appearance of Specimens Quenched from Below and Above Upper Horizontal, × 500. Etched with sodium picrate.

A. Nitrided 75 hours at 500 degrees Cent. (930 degrees Fahr.) then heated for ½ hour in NH_3 at 625 degrees Cent. (1160 degrees Fahr.) and quenched in water. The thin layer is the inner compound; the layer to the right corresponds to the eutectoid layer but is martensitic due to quenching.

B. Nitrided 75 hours at 500 degrees Cent. (960 degrees Fahr.) heated to 685 degrees Cent. (1265 degrees Fahr.) in NH_3 slowly cooled to 625 degrees Cent. (1160 degrees Fahr.) held at this temperature for ½ hour and water quenched. The inner layer darkly etched and showing slip lines is again present having become a good deal wider as a result of the heating to 685 degrees Cent. (1265 degrees Fahr.)

C. Nitrided at 500 degrees Cent. (930 degrees Fahr.) for 75 hours, heated to 685 degrees Cent. (1265 degrees Fahr.) for ½ hour in NH_3 and quenched in water. The inner layer which etches dark with sodium picrate is no longer present.

in Sawyer's diagram. Moreover, the eutectoid structure of this outermost layer is already well marked at temperatures as low as 425 degrees Cent. (see Fig. 10b), much below the temperature of the upper horizontal 660 degrees Cent. In fact, as has just been shown, upon heating to a temperature as high as this the eutectoid structure of the outer layer disappears due to decomposition.

A considerable number of specimens were heated above the temperature of the upper horizontal and slowly cooled, but, as shown in Figs. 14 and 15, no eutectoid could be detected between the two inner nitride layers, as required by Sawyer's diagram. That these specimens had actually passed through a transformation, upon heating to the temperatures used in these tests, was made evident by the disappearance of the inner layer, as shown in Fig. 16c upon quenching the specimens above the transformation temperature. As will be seen from Sawyer's diagram, on the basis of a eutectoid transformation, this inner layer should not disappear on heating to a temperature slightly above the transformation, except at the exact eutectoid composition itself. On the basis of a peritectoid transformation, however, as shown in Fig. 20 the inner layer should disappear entirely on heating through the transformation, as actually occurred. The above evidence, therefore, together with the fact that three layers were found as called for in the construction of a diagram such as Fig. 20, involving a peritectoid transformation, indicated strongly that the upper horizontal represented a peritectoid transformation.

Fig. 17 shows the results of tests made to determine the upper solubility or "stability" limit of the nitride layer which was found to be the most stable one, namely, the yellowish layer not attacked by either picric acid or sodium picrate, and designated by Fry as Nitride I. Upon heating in an atmosphere of ammonia to 785 degrees Cent. (1445 degrees Fahr.) this layer still remained undecomposed, but at 815 degrees Cent. (1500 degrees Fahr.) the structure after quenching showed that decomposition of this layer was practically complete. The solubility or decomposition limit may thus be placed somewhere between the two temperatures, or at about 800 degrees Cent. (1470 degrees Fahr.). Nitride layers are undoubtedly more stable in an atmosphere of ammonia than in the absence of ammonia. Fig. 17d shows the structure of a nitrided specimen, packed in charcoal, heated to 625 degrees Cent. (1155 degrees Fahr.) and slowly cooled. As shown, the two inner nitride layers were still sta-

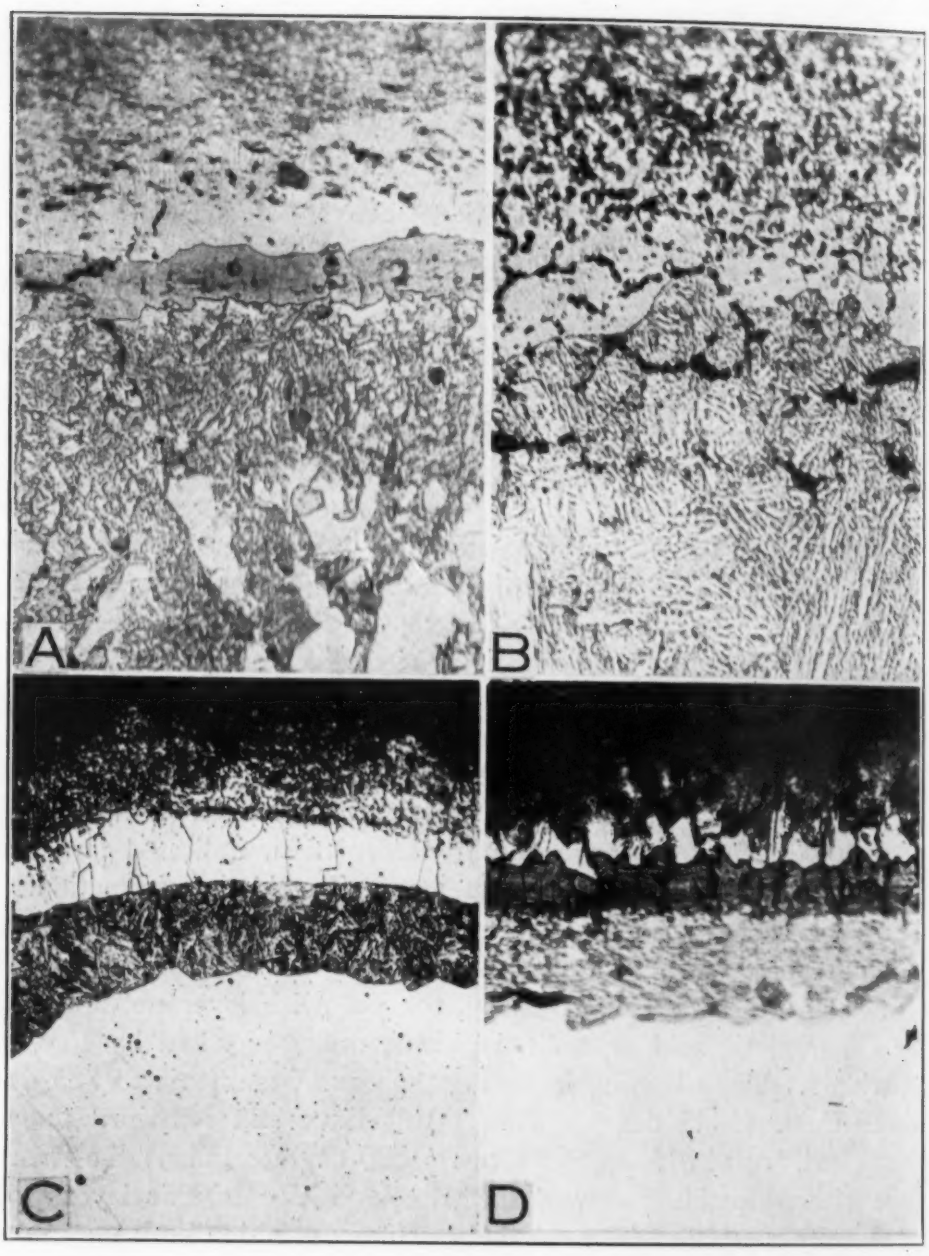

Fig. 17—Determination of Upper Solubility Limit of the More Stable Nitride Layer.
A. Nitrided 75 hours at 500 degrees Cent. (930 degrees Fahr.) then heated in NH_3 at 785 degrees Cent. (1445 degrees Fahr.) for ½ hour and slowly cooled in furnace; etched with sodium picrate. The lighter colored nitride layer is still intact. × 500.
B. Same as A but quenched in water from 785 degrees Cent. (1445 degrees Fahr.) The light colored layer is still intact, × 500.
C. Nitrided 75 hours at 500 degrees Cent. (930 degrees Fahr.) heated ½ hour in NH_3 at 815 degrees Cent. (1500 degrees Fahr.) and quenched in water. The middle layer of the three shown is ferrite indicating decomposition of the nitride layers, × 100.
D. Nitrided 75 hours at 500 degrees Cent. (930 degrees Fahr.) heated ½ hour in charcoal at 625 degrees Cent. (1160 degrees Fahr.) The nitride layers appear to be stable, × 500.

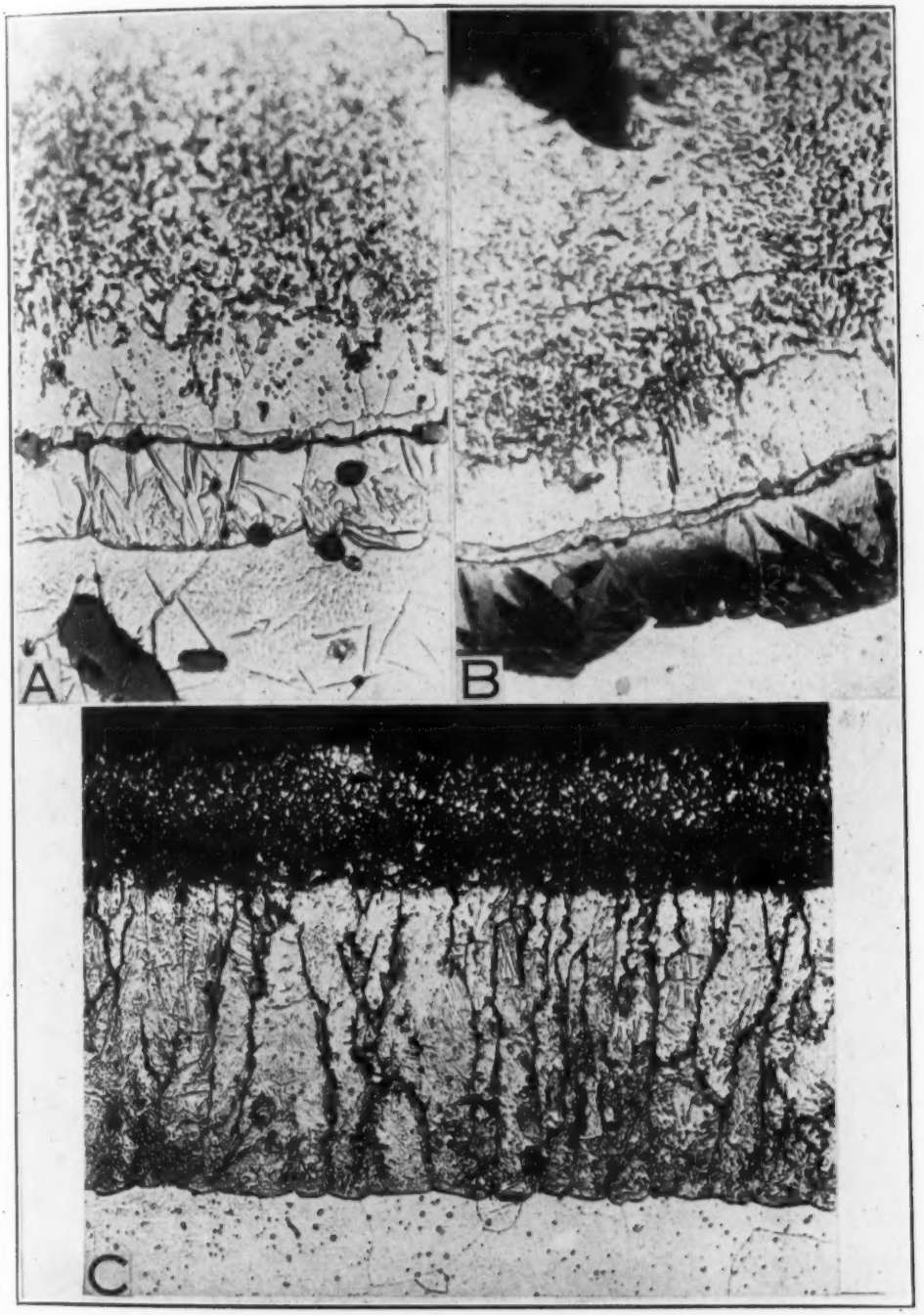

Fig. 18—Martensitic Structures Obtained on Cooling in Air from above Braunite Eutectoid Line.

A. Nitrided 25 hours at 600 degrees Cent. (1110 degrees Fahr.) air-cooled, × 500.
B. Same as A etched with sodium picrate.
C. Nitrided 25 hours at 700 degrees Cent. (1290 degrees Fahr.) and air-cooled, × 100.

Fig. 19—Martensitic Structures Obtained on Cooling in Air from above Braunite Eutectoid Line. Same as Fig. 18c, × 500.

ble at this temperature even in the absence of ammonia. Opportunity has not yet been afforded to make similar tests at higher temperatures.

Figs. 18 and 19 show the martensitic structures which form in the Braunite layer upon fairly rapid cooling in air. The martensitic needles due to nitrogen appear to be exactly similar to those in carbon steel. The structures shown in Fig. 19 also indicate that just as the forms of martensite differ in high and low carbon steels, so in this "nitrogen martensite" the structure toward the higher nitrogen side of the layer is noticeably different from that toward the lower nitrogen side. In high carbon steels, austenite is usually retained with the martensite and analogously in the nitrogen alloy the structure of the higher nitrogen side of the layer shown in Fig. 19, also indicates the presence of an austenitic constituent.

V. X-Ray Diffraction Analyses[16]

X-ray analyses of the crystal structure of several of the specimens of nitrided electrolytic iron granules and of the nitrided electrolytic iron blocks were made, by using a General Electric Company X-ray diffraction apparatus and molybdenum K α radiation. Particles of the nitrided granules which passed through a 100-mesh sieve were examined by the powder method. The diffraction patterns of the blocks were obtained by directing the primary X-ray beam at a small grazing angle with the polished surface. Some nitrided specimens of aluminum-molybdenum nitriding steels, kindly supplied by the Molybdenum Corporation, were also analyzed. Table I gives a summary of the results.

It will be seen in Table I that all the specimens including the steel specimens, gave the hexagonal close packed pattern except the iron specimen No. 39. This one shown in Fig. 18c and Fig. 19, apparently does not contain the intermediate nitride layer discussed in the microscopic examination. The fact that the hexagonal close-packed pattern appeared in the iron specimens nitrided at 600 and 700 degrees Cent. (1111 and 1290 degrees Fahr.) would indicate that the hexagonal close-packed lines which were obtained can not be due entirely to the outermost layer described in the microscopic examination, since, as has been pointed out, this layer is decomposed at these temperatures. On the other hand, it has been shown that the intermediate layer is stable at these and higher temperatures. The

[16]This work was carried out by E. C. Groesbeck and F. Sillers, Jr.

Table I

Results of X-ray Examination of Various Electrolytic Iron and Steel Specimens Nitrided at Different Temperatures

Nitrided Specimen			Nitriding Treatment		Crystal Structure of Nitrided Case as Determined by X-rays (b)
Laboratory No. (a)	Base Material	Form	°C.	Hours	
35	Electrolytic Iron	Block	500	50	H. c. p. and B. c. c.
77	Electrolytic Iron	Block	500	50	H. c. p.
10	Electrolytic Iron	Block	500	75	H. c. p. and B. c. c.
166 T	Al-Mo Steel	Block	500	50	H. c. p.
166 B	Al-Mo Steel	Block	500	50	H. c. p.
E 2	Electrolytic Iron	Powder	540	50	H. c. p.
1000	Electrolytic Iron	Powder	540	50	H. c. p.
7	Electrolytic Iron	Powder	550	2	H. c. p. and B. c. c.
E 3	Al-Mo Steel	sheet 0.017" thick	540	50	H. c. p.
37	Electrolytic Iron	Block	600	25	B. c. c. and H. c. p.
168 T	Al-Mo Steel	Block	600	25	H. c. p.
168 B	Al-Mo Steel	Block	600	25	H. c. p. and B. c. c.
E 1	Electrolytic Iron	Powder	700	25	H. c. p.
39	Electrolytic Iron	Block	700	25	B. c. c. and F. c. c.
170 T	Al-Mo Steel	Block	700	25	B. c. c.; F. c. c.; (and H. c. p.)
170 B	Al-Mo Steel	Block	700	25	B. c. c.; F. c. c.; (and H. c. p.)
E 4	Al-Mo Steel	sheet 0.017" thick	700	25	H. c. p. and B. c. c.

(a) The T and B after these specimen numbers in this column stand for the top and bottom faces of the block specimens in question.

(b) H. c. p. = hexagonal close-packed; B. c. c. = body-centered cubic; F. c. c. = face-centered cubic. In the cases where more than one crystal structure is present, the more pronounced one is placed first. The structure reported in parentheses was present only to a small extent.

hexagonal close-packed pattern was also considered as not being due to the inner one of the three nitride layers. It appeared more probable that this innermost layer has a face-centered cubic lattice, since it shows a twinned structure and the presence of this crystal structure was indicated, though not definitely determined, in the X-ray spectrograms. The indications, are therefore, that the hexagonal close-packed pattern was due to the intermediate one of the three nitride layers.

In the discussion of the tentative iron-nitrogen diagram, which follows, the intermediate layer has been assigned the composition Fe_4N. There is, therefore, disagreement with the results reported by Hagg[17] who, in X-ray analyses of nitrided pure iron obtained by reducing powdered iron oxide with hydrogen and nitriding the iron in the usual way, has given evidence indicating that the compound Fe_4N is face-centered cubic. Results similar to those obtained by

[17] G. Hagg: X-ray Studies on the Nitrides of Iron, *Nature*, Vol. 121, 1928, p. 826.

Hagg appear to have been obtained by other investigators[18], but the X-ray data available at present appear to be insufficient to definitely decide the matter. It should be noted that no doubt is cast on the result obtained by Hagg that the compound Fe_2N is hexagonal close packed and it may perhaps be suggested, in view of the very marked increase in the lattice parameter of the hexagonal close-packed patterns shown by him between the specimens of 6.1 and 11.3 per cent nitrogen content, that the compounds Fe_4N and Fe_2N both have hexagonal close-packed patterns, the latter having the greater parameter[19].

It seems probable that the discrepancies in interpretation of the X-ray data are more apparent than real. Since Fry's diagram, which has probably been used as the basis for interpretation, does not recognize the presence of Fe_6N, the inner nitride layer is presumably taken by other workers as Fe_4N. If Fe_6N is admitted to be present the discrepancies lie in the interpretation, not in the observations. Here again, as in the thermal analysis, interpretation is difficult because of the heterogeneous nature of the specimens and of inability to isolate one layer at a time for study.

Reference was made above to some undetermined lines that were noted in the X-ray spectrograms (not indicated in Table I). These lines apparently represented two different parameters of the face-centered cubic lattice. It may perhaps be suggested that one set of these lines is due to the innermost layer described in the microscopic examination and assigned the composition Fe_6N in the tentative iron-nitrogen diagram, shown in Fig. 20, and the other to rapidly cooled Braunite which was present in some of the specimens and might be expected to give a face-centered cubic pattern, analogous to that of austenite in quenched high carbon steel.

VI. Tentative Iron-Nitrogen Diagram

The tentative diagram which has been drawn as a result of the study described above is shown in Fig. 20. It should be remembered that this diagram is not an "equilibrium" diagram, as the term is generally used. The iron-nitrogen alloys are unstable and equilibrium

[18]R. Brill: The Crystal Lattice of Fe_4N. *Z. Krist.*, Vol. 68, 1928, p. 379; *Chemical Abstracts*, Vol. 23, May 10, 1929, p. 2083. G. Osawa; S. Iwaizumi. X-ray Investigation of Iron-Nitrogen Alloys. *Z. Krist.* Vol. 69, (1928) p. 26-34; *Chemical Abstracts*, Vol. 23, 1929, p. 2408.

[19]The lattice parameters for the crystal structures given in Table I have not yet been accurately worked out but these results will be given in the forthcoming Bureau of Standards Research Paper on this subject.

conditions cannot be determined without taking account of the pressure of nitrogen in the system and the activity of the nitrogen, i. e., whether it is atomic or nascent, or molecular. For instance, the temperature of the point D in the diagram, showing the stability limit of the compound Fe_4N, which was determined upon heating in ammonia gas, would undoubtedly be considerably lower in vacuum. It

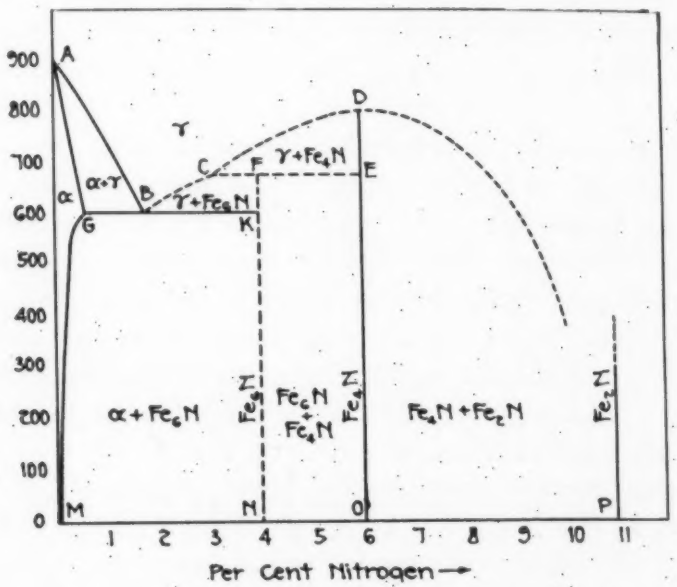

Fig. 20—Tentative Iron-Nitrogen Diagram.

was even suspected during the work that since the arrests during the thermal analyses were obtained on heating and not on cooling, most of the nitrogen being evolved during the run, they might be due entirely to decomposition and not to transformations between the solid constituents. However, in measurements of the pressure of the gas evolved on heating nitrided specimens of a wide range of average nitrogen content it was found that the pressures increased continuously and not in two stages corresponding to the two thermal transformations. This indicated that the latter were not due solely to decomposition. A detailed report of these experiments will be given in the forthcoming Bureau of Standards Research Paper on the subject. That the thermal arrests represented transformations between the solid constituents was, of course, indicated by the microscopic examination. It may also be mentioned that, since the nitrided specimens were prepared by the diffusion of nitrogen and not by melting, the composition gradients are not smooth but occur in

steps between adjacent nitrided layers. As called for by the rules governing the construction of equilibrium diagrams, a duplex field marked $Fe_6N + Fe_4N$ has been indicated in the diagram, but actually there are no signs of such a field in the microstructure, the compounds lying directly adjacent to each other. A similar result obtained in the diffusion of melted zinc into solid copper at 450 degrees Cent. (840 degrees Fahr.) has been described by Hudson.[20]

As shown in Fig. 20 the outer, intermediate, and inner layers noted in the microstructure have been designated as the compounds Fe_2N, Fe_4N, and Fe_6N respectively. No chemical analyses of the compositions of the individual nitride layers were made, as they could not be sharply separated, and stoichiometric relations such as those of Noyes and Smith[21] who reported Fe_2N, Fe_4N, Fe_6N, and Fe_8N as possible compounds, were used as the principal guide for setting the compositions of the layers. This construction is a modification of Fry's diagram which showed only two layers, Nitride I and Nitride II. The intermediate layer described in the microscopic examination is the one which corresponds in microstructure to Fry's Nitride I and it should be noted Fry designated this layer as Fe_2N whereas in this diagram it is designated Fe_4N.

This departure from Fry's diagram appears to be justified by the fact that the outer layer described in the microscopic examination was not noted by Fry and because the construction shown fits in with the thermal analyses obtained by Sawyer and in this work. Moreover, on the grounds of Fry's own observations it would appear better to designate his Nitride I (corresponding with the intermediate layer described in this study) as Fe_4N, instead of Fe_2N. The layer, Nitride I, in Fry's micrographs is shown to be stable at the nitriding temperature of 680 degrees Cent. (1255 degrees Fahr.) which he used, whereas his diagram indicates the compound Fe_2N to be unstable at comparatively low temperatures.

The outermost layer has been designated as Fe_2N, but since it has a two-phase eutectoid-like structure it may be considered as a eutectoid between the compounds Fe_4N and Fe_2N, the eutectoid transformation probably occurring below 425 degrees Cent. (795 degrees Fahr.) as indicated by Fig. 10f in which the eutectoid structure is present upon nitriding at that temperature. There is, how-

[20]O. F. Hudson: The Critical Point at 460° C. in Zinc-Copper Alloys, *Journal*, Institute of Metals, Vol. 12, No. 2, 1914, p. 89.

[21]A. A. Noyes and L. B. Smith: The Dissociation Pressure of Iron-Nitrides, *Journal*, American Chemical Society, Vol. 43, 1921, No. 1, p. 475.

ever, no indication of such a eutectoid in the thermal analysis curves. Further study of the alloys between 6 and 11 per cent nitrogen would be required to clear up this point.

From the results of Noyes and Smith the innermost layer might have been designated either Fe_6N or Fe_8N, since they consider both are possible. However, a vertical line corresponding to the compound Fe_8N of approximately 3 per cent nitrogen content would meet the upper horizontal at the point C, in which case the lines BC, CD, and CE, would all meet the vertical line of the compound at the point C. As this did not appear probable, the compound Fe_6N was chosen to designate the innermost layer.

The reasons for modifying Fry's and Sawyer's diagrams by the peritectoid horizontal CE have already been given. For the solid solubility line, MG, Fry's diagram has been followed although it would appear that the solid solubility at the eutectoid temperature, namely the point G, is not very definitely established. The temperatures for the lower eutectoid horizontal GK, 600 degrees Cent. (1111 degrees Fahr.) and the upper peritectoid horizontal CE, 675 degrees Cent. (1245 degrees Fahr.) are taken as rounded figures, from the results of Sawyer, Fry, and those obtained in this study.

Fry's temperature scale has been regarded as about 10 degrees too low[22] and this was considered in setting the temperature of the eutectoid horizontal at 600 degrees Cent. (1111 degrees Fahr.). It will be noted that the point C at 3 per cent nitrogen content at which composition the upper horizontal begins is at a considerably higher nitrogen content than the composition at which the upper horizontal first appeared in the thermal analyses. As shown in Fig. 5 this was at 1.25 per cent. As has already been stated, however, the nitrogen content in the nitrided layers in this composition range appeared to be about three times the average nitrogen content. The location of the point C for the beginning of the upper horizontal is, therefore, in fair agreement with the thermal analysis results.

Since in the Bureau of Standards work the peritectoid transformation was completed below 675 degrees Cent. (1245 degrees Fahr.) in a large majority of the cases and always began below 660 degrees Cent. (1220 degrees Fahr.) it is possible that the rounded figure of 675 degrees Cent. (1245 degrees Fahr.) is a trifle high.

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[22] A. Bramley and F. W. Haywood: Determination of the Iron-Iron Nitride Eutectoid, Carnegie Scholarship Memoirs 17, 1928, p. 76.

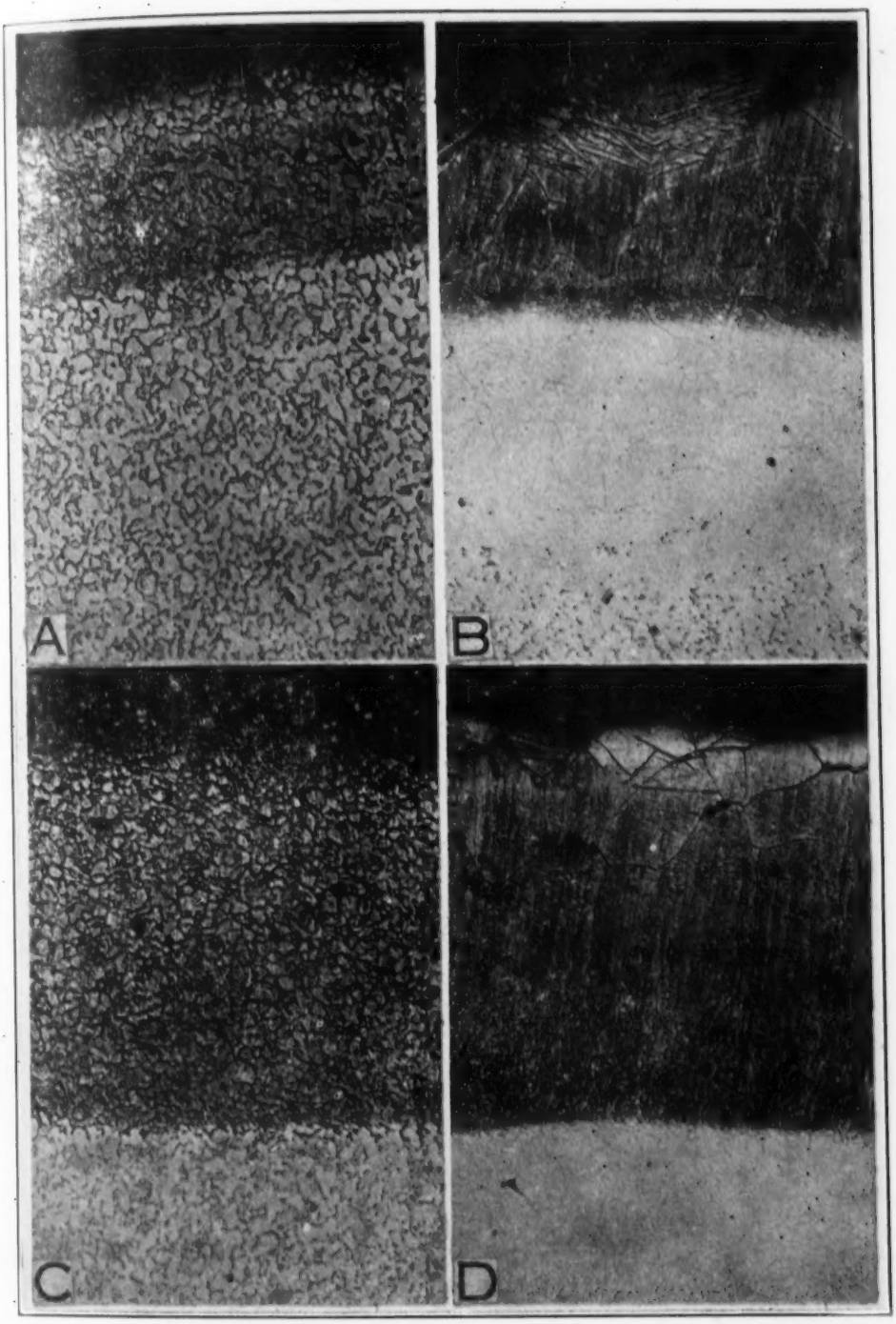


Fig. 21—Nitrided Layers in Special Aluminum-Molybdenum Nitriding Steels, × 100.
A. Nitrided 50 hours at 500 degrees Cent. (930 degrees Fahr.) the original structure can still be discerned in the nitrided layer. There is only one layer. No nitride needles were detected in the cores of any of the nitrided steels.
B. Same as specimen A but at edge decarburized before nitriding.
C. Nitrided 25 hours at 600 degrees Cent. (1110 degrees Fahr.) The nitrided layer is deeper than in "A" or "B" because of the higher temperature of nitriding.
D. Same as specimen "C", but at decarburized edge. Slip lines are present in the coarse crystals, but they are not so numerous as in "B", nitrided at the lower temperature.

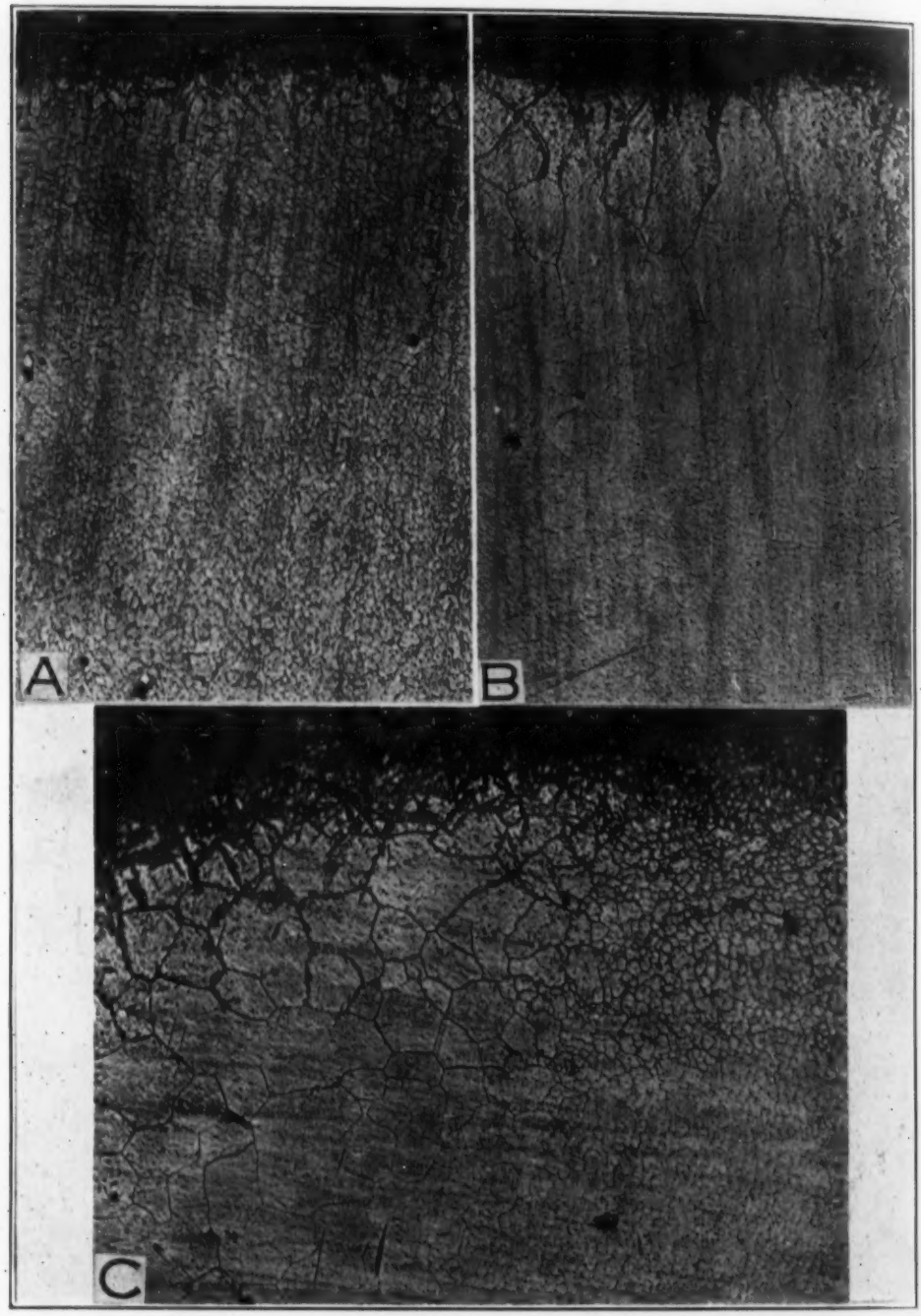


Fig. 22—Structure of Steel Specimens Nitrided 25 Hours at 700 degrees Cent. (1290 degrees Fahr.), × 100.

A. Fine grain at undecarburized edge of block.

B. Coarse grain at decarburized edge of block; at this high nitriding temperature, however, no slip lines appeared.

C. Juncture of decarburized and undecarburized edge; Note the intergranular darker constituent which appears at this nitriding temperature.

Fig. 23—Slip Lines in Nitrided Layers. × 500. Nitrided 25 hours at 540 degrees Cent. (1005 degrees Fahr.)

A. Note number of slip or check lines toward the interior. These slip lines were found to be present very close to the core.

B. This specimen contained no molybdenum.

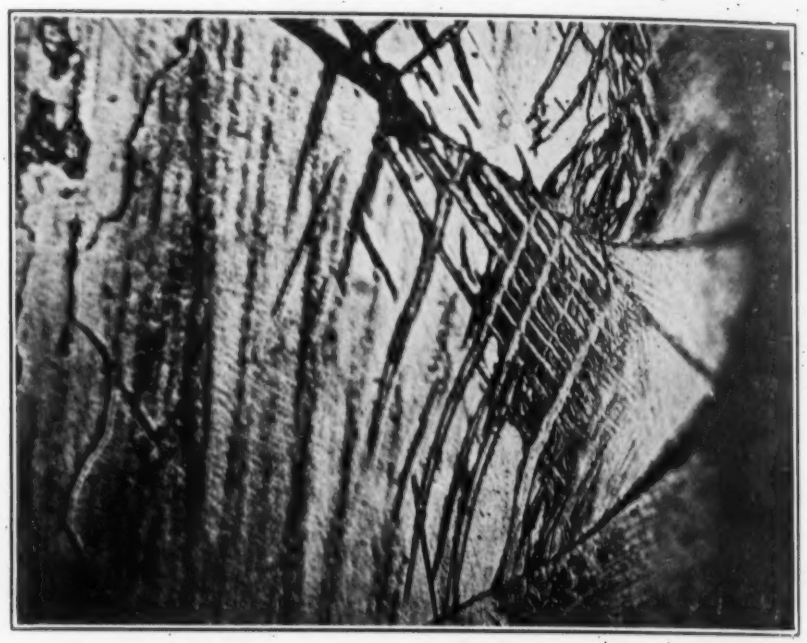


Fig. 24—Slightly Rounded Twins and Slip Lines in Coarse-Grained Nitrided Layer. × 500.
Nitrided 25 hours at 540 degrees Cent. (1005 degrees Fahr.); at the decarburized edge of the block.

VII. Observations on the Structure of Nitriding Steels

The aluminum-molybdenum nitriding steels mentioned in connection with the X-ray analyses were also examined under the microscope. They contained 2.5 per cent aluminum, 0.85 per cent molybdenum and carbon 0.25, except one of the specimens (see Fig. 23) which contained no molybdenum and 0.50 per cent carbon. As may be seen in Fig. 21, the steel specimens, unlike the nitrided iron specimens, showed only one nitrided layer, which was of a yellowish color darkened brown by etching with picric acid. The original structure of the steels is not changed to any degree by the nitriding and may be discerned in the nitrided layer, as shown in Fig. 21a. Even in specimens of nitrided sheet of this material, the original worked structure still remained, the nitriding being evident in the microstructure only by the yellowish tinge of the nitrided layer. In none of the steel specimens including those which were heated to 725 degrees Cent. (1335 degrees Fahr.) was there any evidence of a eutectoid layer corresponding to Braunite. The steel specimens also differed from the nitrided iron specimens in that in the former no nitride needles were present in the case, which is, of course, import-

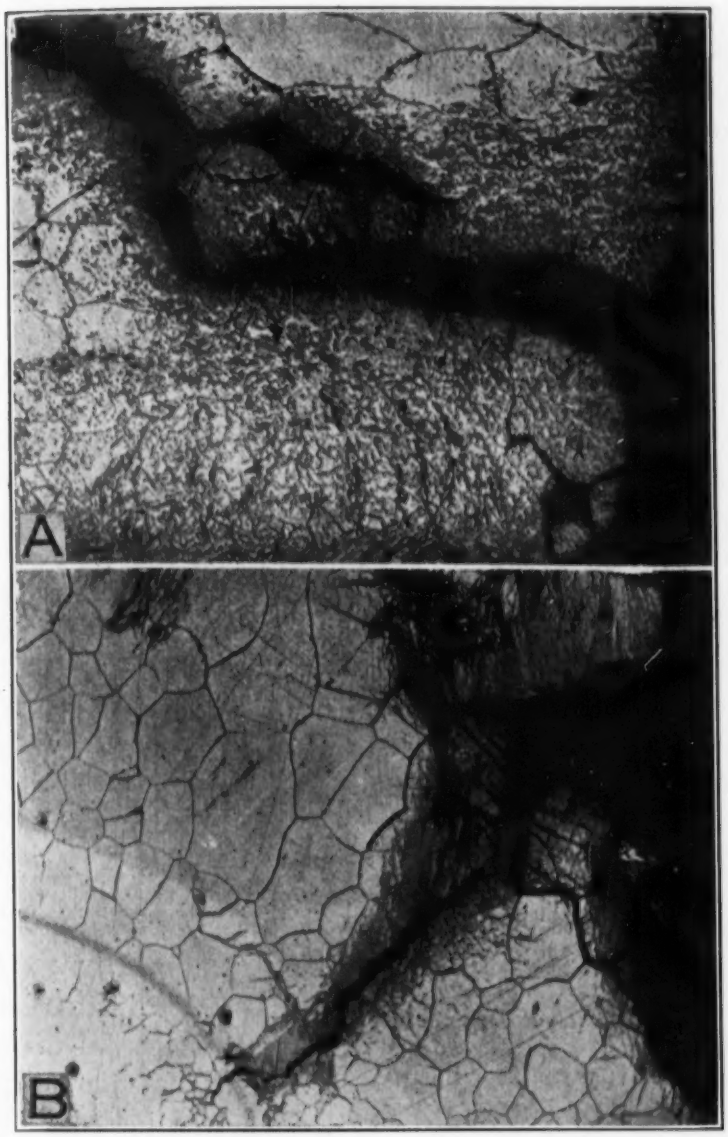


Fig. 25—Fissures and Darker Etching Constituent in Nitrided Specimen Heated to 725 degrees Cent. (1335 degrees Fahr.) in NH_3, × 500.
A. Nitrided 25 hours at 600 degrees Cent. (1110 degrees Fahr.), then heated 1 hour in NH_3 at 725 degrees Cent. (1335 degrees Fahr.)
B. Nitrided 25 hours at 700 degrees Cent. (1290 degrees Fahr.), then heated 1 hour in NH_3 at 725 degrees Cent. (1335 degrees Fahr.)

ant on account of the embrittling effect of the nitride needles. The absence of nitride needles in the nitriding steels is readily explained by the fact that only one nitrided layer is present. As was pointed out by Fry and observed in the microscopic examination of the nitrided iron specimens, the familiar nitride needles are evidently due

to the innermost layer, which is not formed in these special alloy steels used for commercial nitriding.

The steel specimens were nitrided at 500, 600 and 700 degrees Cent. (930, 1111, and 1290 degrees Fahr.) respectively. Those nitrided at the lower temperatures appeared to be more brittle than those nitrided at the higher temperatures. The specimens were in the form of blocks, one edge of which had been decarburized before nitriding. In these decarburized edges of the specimens the grain size was comparatively large and in the specimens nitrided at the lower temperatures these large grained areas showed profuse twinning and slip line formation, as shown in Figs. 21, b and d and in Fig. 24. In the specimens nitrided at the higher temperatures, however, the slip lines did not appear to any marked degree as shown in Fig. 22 b and c. Moreover, in the fine-grained areas slip lines or twins were practically absent even in those nitrided at the lower temperatures as shown in Figs. 21 a and c. Since the slip lines which formed in the large grained areas are evidently an indication of brittleness it is apparent that the presence of surface decarburization in nitriding steel should be guarded against. Due to the extreme hardness of the nitrided layer particularly at the surface it would be expected to be very brittle. It was observed, as shown in Fig. 23, in specimens in which the nitrided layer was tapered off gradually by grinding, that large numbers of slip or check lines were also present very close to the core. This is especially apparent in the specimen shown in Fig. 23 a.

Two of the specimens were heated to 725 degrees Cent. (1335 degrees Fahr.) in ammonia for 1 hour. After this treatment, as shown in Fig. 25 the nitrided layers gave evidence of the presence of another constituent which was etched slightly darker than the matrix by sodium picrate. Fissuring of a type probably similar to that described by Vanick, Sveshnikoff, and Thompson[23] also occurred. These authors concluded that fissuring was generally preceded by decarburization.

It was observed that the fissuring of these specimens was also much more pronounced in the edges of the specimens which had become decarburized before nitriding.

In the X-ray analyses summarized in Table I, the steel specimens nitrided at 700 degrees Cent. (1290 degrees Fahr.) showed

[23]J. S. Vanick; W. W. Sveshnikoff; and J. G. Thompson: Deterioration of Steel in the Synthesis of Ammonia, Bureau of Standards, Technologic Paper 361.

more than one crystal pattern, whereas those nitrided at the lower temperatures, showed only one pattern, namely, the hexagonal close packed. Under the microscope also, as shown in Fig. 22, another constituent was noticed, present as a grain boundary network. This result is of some interest, since nitrided articles have been suggested for use at comparatively high temperatures, and it would appear necesary to obtain assurance of the stability of the different nitriding steels at these temperatures.

Summary

In a study of the iron-nitrogen system, thermal analyses, microscopic examinations, and X-ray analyses were made of nitrided electrolytic iron specimens. From the data obtained and with the two existing diagrams of Sawyer and Fry as a basis a modified iron-nitrogen constitution diagram has been tentatively drawn.

The thermal analyses appeared to confirm those of Sawyer which indicated that there are two temperature horizontals on the high nitrogen side of the diagram, but the microscopic examination indicated that the upper horizontal represented a peritectoid reaction, and not a eutectoid transformation as Sawyer supposed.

Three iron-nitride layers were observed, whereas Fry had noted only two. The outer, intermediate, and inner layers have been designated at Fe_2N, Fe_4N, and Fe_6N respectively.

In X-ray analyses a hexagonal close packed pattern and indications of a face-centered cubic pattern were obtained. According to the microstructure of the layers it appeared probable that the face-centered lattice was due to the inner layer Fe_6N and the hexagonal close packed pattern to the intermediate layer Fe_4N; this is not in agreement with the interpretation of X-ray data by Hagg and other investigators who ascribe the face-centered cubic lines to Fe_4N. The data available at present do not appear to be sufficient to definitely decide the matter.

Observations on several nitrided specimens of aluminum molybdenum nitriding steel were also made. Those nitrided at the usual nitriding temperatures contained only one layer and showed a hexagonal close packed pattern.

Acknowledgement

The author wishes to express his indebtedness to H. O. Willier

for his conscientious and efficient aid in the nitriding of a large number of specimens and the metallographic work on them.

DISCUSSION

Written Discussion: By O. E. Harder, University of Minnesota, Minneapolis, Minn.

I have studied Mr. Epstein's paper in considerable detail. I think his interpretation of results and his tentative iron-nitrogen diagram are quite reasonable. I have observed microstructures similar to those reported in his paper, but have not given them the detailed study which he has. It seems that it might be possible in further study of this diagram to continue the nitriding operation over a longer period of time and, by the use of different temperatures, obtain more of the particular constituent. His observations regarding the solubility of nitrogen, or as indicated in his diagram the nitride Fe_8N in iron, seem to be entirely in keeping with one of the observations in connection with commercial practice. It is known that nitrided products, while they are cooling down from the nitriding temperature, are much softer than they are when finally cooled down to room temperature. This seems to indicate that precipitation hardening is in progress. This may be an interesting subject for further study. The eutectoid structure near the outer rim suggests the presence of a second eutectoid, that is a eutectoid between Fe_4N and Fe_2N. If these different nitrides could be obtained in a more nearly pure form by controlling the time and temperature of nitriding, it seems that some of the questions regarding the space lattice could be cleared up.

Mr. Epstein's X-ray results are not in agreement with those by Osawa and Iwaizumi published in the Scientific Reports of the Tohoku Imperial University, Series I, vol. 18, No. 1. Mr. Epstein attributed the hexagonal close-packed pattern to Fe_4N while the Japanese investigators attributed this pattern to Fe_2N. They determined the lattice constant as 2.743 and the c/a ratio as 1.59. The method used by Mr. Epstein in making his X-ray determinations would seem to make it possible to have an X-ray pattern to represent the outer layer of the nitrided case and therefore a material of high nitrogen content in which the compound Fe_2N might predominate. Osawa and Iwaizumi did not recognize the compound Fe_8N but did study the compound Fe_4N which they identified as having the face-centered cubic lattice with a nitrogen atom at the center of each elementary cube. The unit parameter determined was 3.86Å. The presence of the face-centered cubic lattice characteristic of austenite, and the enlarged parameter as compared with austenite, suggest a solid solution, although this is a part of the problem which requires further investigation. The paper by Osawa and Iwaizumi does not give details on the preparation of specimens except as to nitrogen content, and it is not possible to know at what temperature these specimens were nitrided and the rate of cooling. I think it may be expected

that specimens which have been rather rapidly cooled from the field of gamma iron may retain that pattern and, even though the nitrogen compound separates out on cooling, we still have the possibility that the particles will be too small to produce a definite X-ray pattern. The same remarks apply to specimens representing the α solid solution because the precipitated phase in this field may fail to give an X-ray pattern.

In conclusion, as Mr. Epstein points out, the experimental evidence submitted is not as complete as is desirable, but it seems to be a very valuable contribution and his tentative diagram seems reasonable and will be helpful in further studies.

Written Discussion: By V. O. Homerberg, Massachusetts Institute of Technology, Cambridge, Mass.

Mr. Epstein's excellent contribution to this important subject is an opportune one not only because of its bearing on the ever increasing importance of nitriding as applied to certain alloy steels, but also because of the presence of Dr. Fry and Dr. Sawyer at this meeting. The author refers quite frequently to the previous work of these two investigators.

A study of nitrided material is beset with difficulties for reasons as given by the author. Dr. Sawyer conducted his investigation at the Massachusetts Institute of Technology under the guidance of Dr. Fay. It was my good fortune to have been in close contact with Dr. Sawyer at that time. The difficulties which he encountered and the patience and the careful work exhibited by him in his investigation are greatly to his credit. In view of the many difficulties encountered in an investigation of this kind, especially because of the difficulty of procuring homogeneous samples, it is gratifying to note the confirmation by Mr. Epstein of many of the results obtained by Dr. Fry and Dr. Sawyer.

The author's discussion of the presence of a peritectoid seems to be well substantiated by his observations including thermal data and microscopic studies. The microstructures are similar in many respects to those published by Dr. Fry.

The observations in a study of the structures obtained by nitriding special alloy steels are interesting and are mainly in accord with those noted by various investigators. The presence of a needle-like structure at the surface very often accompanies decarburization. However, it sometimes happens that a white layer is formed which does not show any needles or ferrite grain boundaries. This layer is extremely hard and brittle and reacts with etching reagents in the same manner as the white net-work. Dr. Walsted and I have stated in our paper that the two structures very likely represent the same constituent. It is believed that this constituent is an iron nitride or a complex one of iron and one or more of the alloying elements.

It is to be hoped that this valuable contribution by Mr. Epstein will be followed by further observations on the structure of nitrided steels.

Written Discussion: By C. B. Sawyer, Ph. D., Brush Laboratories, Cleveland.

After reading Mr. Epstein's paper, I am impressed anew with the

difficulties attending the study of the iron-nitrogen equilibrium diagram. Only those who have actually sought to sift its vagaries and fix its limits can appreciate the bewildering aspect which the problem can present. Mr. Epstein is to be congratulated on his very able paper.

Mr. Epstein has kindly referred to my early work with iron and nitrogen, and states that the Bureau of Standards began its investigation in 1922, before either Sawyer's or Fry's work was published. In the interests of accuracy I should like to bring out that my work was made available to the public in June of 1921 as a thesis presented to the Massachusetts Institute of Technology.

No mention of either my work begun in 1919, or Hurum's which preceded it, should omit the name of Professor Henry Fay, who stimulated and aided in every way both of these researches. He was fully aware of the general possibilities residing in the study of nitrogen in steel, and it is a matter of enduring loss that illness should have kept one of our most brilliant metallurgists and teachers from continuing in this field.

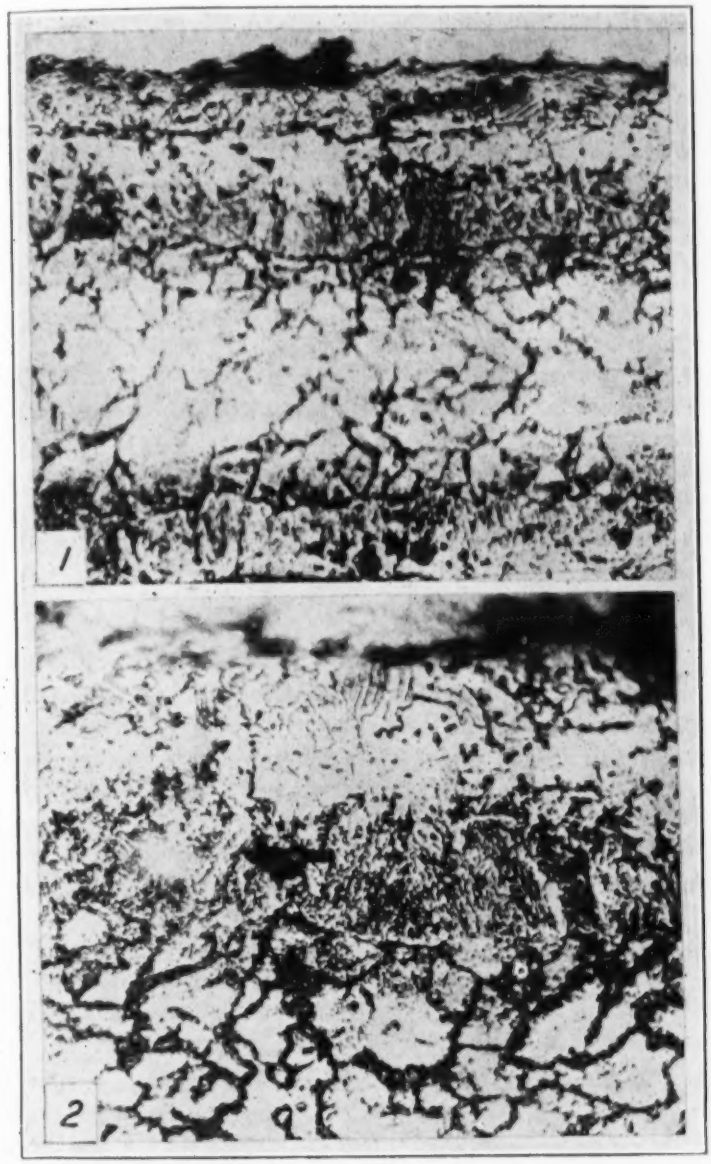
It is, of course, gratifying to have Mr. Epstein's confirmation of these early thermal analyses. One can no longer doubt that the two thermal arrests observed by me are real transition points, not due to decomposition effects as had been stated. Even the rather indefinite low temperature swings described in my work appear to have some counterpart in Mr. Epstein's results.

Mr. Epstein has added valuable information, and the new or outer eutectoid deserves special mention. In accounting for his observations, he has found it most satisfactory to postulate two inner compounds and a peritectoid transition. I believe, however, that there are to be found in his photomicrographs and X-ray data some evidence of still another compound with a corresponding eutectoid in place of the peritectoid which he prefers. I have considerable hesitation in advancing an interpretation differing from Mr. Epstein's and only do so because of the universally admitted uncertainty and difficulty in dealing with this diagram.

Of the photomicrographs susceptible to this different interpretation the one marked B in Fig. 14 of Mr. Epstein's paper is most suited for discussion. This is of a nitrided and annealed iron block etched with sodium picrate. The bottom layer of this photomicrograph, where the letter B appears, is clearly braunite, the first eutectoid. Above this braunite layer is a narrow white region which according to my interpretation may be designated as the compound Fe_3N. Immediately above is a very dark layer somewhat suggesting a second eutectoid, followed by a grayish layer to which the formula Fe_6N might be assigned. The very dark layer would then be an eutectoid between Fe_3N and Fe_6N. Immediately above the Fe_6N grayish layer, and divided from it by a sharp boundary, is a white layer which may be called Fe_4N. Above the Fe_6N layer is the decomposed residue of Mr. Epstein's new eutectoid between Fe_4N and Fe_2N.

Mr. Epstein has himself mentioned some undetermined lines noted in the X-ray spectrogram.

Realizing the inadequacy of the grounds so far presented on which to rest the above interpretation, I have attempted to gather more evidence



Figs. 1 and 2—Cross Section of Disk Nitrided 3½ Hours at 1220 Degrees Fahr. Center Portion Thought to be Fe_8N. Eutectoid Supposed to be Fe_8N and Fe_4N lines on each side of Center.

and submit two new photomicrographs taken from samples made during my 1921 work. Fig. 1, of this discussion taken at a magnification of about 250 diameters shows the entire cross section of a nitrided disk of

very low carbon sheet iron 0.228 millimeters thick. This disk was nitrided in ammonia which circulated freely about it and penetrated from both sides. The time allowed was three and one-half hours at a temperature of 1220 degrees Fahr. (660 degrees Cent.) or slightly higher; being thus just above the second transition point as determined by Mr. Epstein. After nitriding, the specimen was furnace-cooled in ammonia, though the time required was less than customary. The nitrided disk contained about 4.5 per cent nitrogen.

This specimen, etched with nital, shows a light colored center, thought to be Fe_8N, with a eutectoidal structure adjoining it and supposed to consist of Fe_8N and Fe_6N. Above this lies a white layer to which is assigned the formula Fe_6N, separated by a sharp boundary from the outermost layer Fe_4N, containing slip planes and twins.

Fig. 2 is of the same specimen, but at about 500 diameters. The eutectoidal appearance is much more clearly shown and merges gradually into the white layers on each side. The outermost layer supposed to be Fe_4N again shows slip planes and twins.

It has been suggested that the center of the disk is ferrite rather than a compound of nitrogen and iron. That this is not the case is indicated by several factors. First, under the conditions of heating, the grain size of the original ferrite should not be changed; but there has actually been considerable refinement. Second, on heating the disk to about 1380 degrees Fahr. (750 degrees Cent.) for 5 minutes, and furnace cooling in an atmosphere of air, thus bringing about decomposition, the center portion changed to braunite. Possibly though, this could be brought about by diffusion of nitrogen. Third, the etching characteristics of the original center portion are not those of ferrite. Boiling sodium picrate apparently turns it yellow. Ten per cent nital leaves it unaltered after two and a half minutes, though a pure ferrite disk was deeply etched in half a minute. If held, during etching, with metal crucible tongs, the rate of etching of the nitrided disk can be greatly accelerated and, depending on the time, the center portion etched lightly so as to appear like ferrite, or more heavily so as to be uniformly blackened over its whole surface. This effect is very striking.

More work is required to give weight to the suggestions advanced here, and it is hoped that someone will wish to carry on this research. In conclusion I wish to thank Mr. Epstein for the interest he has taken in these remarks and his courteous attention.

Written Discussion: By Dr. H. H. Lester, Watertown Arsenal Watertown, Mass.

Mr. Epstein is to be commended most highly for the excellent results obtained under most trying experimental difficulties. The writer tried at one time to analyze some data from nitrided pure iron wire, but gave up the study because of difficulties encountered. X-ray analysis however, showed one or possibly two hexagonal structures and a body-centered structure. The structures did not correspond closely with structures found in aluminum and nickel steels.

The author points out that nitrogen may cause the formation of martensite under proper conditions. This would indicate a relatively high nitrogen solubility in gamma iron with a large change in solubility in passing through the A_3 point. It might indicate also that these cases are subject to modification by thermal treatment.

It occurs to me that perhaps the critical point for nitriding alloys may be 1075 degrees Fahr. (580 degrees Cent.) or lower when nitrified, that the surface of such steel having been transformed might absorb more nitrogen and hold it in solution than would saturate the alpha phase and that such a surface quenched or quenched and subsequently tempered might show improved qualities in the case.

A question of importance is what are the effects of carbon and of various other steel constituents on the absorption of nitrogen. Mr. Epstein's work is suggestive of a wide field of research.

Written Discussion: By H. W. McQuaid, Timken Detroit Axle Co., Detroit.

Mr. Epstein is to be congratulated upon the contribution he has made to the scientific study of the iron-nitrogen system. The amount of work which has been necessary in order to complete such a paper is without doubt enormous.

The same can be said of the papers by Messrs. Harder, Gow, and Willey, and by Messrs. Homerberg and Walsted; all of which indicate that many hours of pains-taking effort has been given to the relatively new art of nitriding. Mr. Epstein's paper, which is limited to the field of pure science, furnishes data which is a necessary basis to the proper building up of a knowledge of the nitriding art. There is no doubt but what contributions of the pure science should precede to building up of any art, and researches such as Mr. Epstein's are seldom given the attention which they really merit.

While the work done by Mr. Epstein, and the conclusions drawn seem above criticism to me, there is a little doubt in my mind as to whether or not the stability of the iron nitrides in the presence of an excess of hydrogen or nitrogen would not affect the results, so as to make them erratic. Newton Friend has shown that iron nitride is unstable in the presence of an excess of either hydrogen or nitrogen and I am wondering whether the dissociation obtained in nitriding the samples or the effect of the nitrogen atmosphere should not receive very careful consideration.

Oral Discussion

W. J. MERTEN: Mr. Epstein's comprehensive paper on the constitutional diagram of iron nitrides and the lengthy discussions, involving iron nitrides has raised a question in my mind and I know in the minds of others who have done considerable work on nitriding of alloy steels, whether the points brought out are really pertinent to the nitriding problem. We are dealing with complex alloys and very probably with complex nitrides and not with simple iron nitrides. That this is the case is clearly indicated

by the difference in microstructure and reaction towards nitriding of the molybdenum-aluminum alloy steel as compared with aluminum-chromium steels. The difference in physical properties of the nitrided case of the former as well as the greater temperature range of nitriding without variation in results is so marked that investigation along this line suggests itself.

With reference to the white, extremely hard and brittle surface layer it will be found that long time exposure accompanied by decrease in rate of dispersion and probably increase in rate of nitride formation causes a surface concentration of nitrides. This layer has not been found in molybdenum-aluminum steel nor is it found on short time nitriding of aluminum-chromium steels.

N. A. ZIEGLER: I would like to ask Mr. Epstein two questions. The first is whether or not all iron-nitrogen alloys are being decomposed by heating in atmospheric air. I understood that some of the iron-nitrogen alloys are decomposed. If this is the case, then iron-nitrogen system should not be considered as a stable system but as a case of metastable equilibrium. The other thing I am interested in is whether or not the iron-nitrogen alloys would be decomposed by vacuum melting unless some kind of deoxidizer is added to the charge. I would like to ask Mr. Epstein if this is the case with iron-nitrogen alloys as well.

A. B. KINZEL: I should like to point out that in the work on the aluminum containing steels at the Union Carbide and Carbon research laboratories Mr. Vilella has developed an etch which brings out the constituents very much more satisfactorily than etches used in the past. With this etch we find three distinct layers in the aluminum type steel on nitriding in the usual manner at sub-eutectoid temperatures. These are found in the identical specimens which show only one layer when etched with picric or nitric acid. This will, undoubtedly have a distinct bearing on the conclusions to be drawn from Mr. Epstein's work pertaining to the alloy steels which are being recommended for use in nitriding. I shall not describe this etching reagent at this time as we expect to publish a full account of it in the near future.

Author's Reply

I deeply appreciate the comments made by those who have taken part in the discussion. Dr. Lester's, Dr. Homerberg's and Mr. McQuaid's remarks require only grateful acknowledgment. Dr. Harder mentions the disagreement between the X-ray results reported in the paper and those obtained by other investigators. These discrepancies were noted in the paper and it was there suggested that they were probably due to differences in interpretation arising out of the inability to isolate the iron nitride layers.

I am very glad indeed to have Dr. Sawyer's viewpoint presented. I do not agree with him, however, that the photomicrographs shown in the paper can justifiably be interpreted to mean that there are any other iron nitride layers present than the three which were discussed.

Neither do I feel that the photomicrographs Dr. Sawyer has shown in his discussion indicate the presence of additional layers. However, these questions can hardly be settled definitely by going over what has been done; the answer will come only from further work on the subject.

In reply to Dr. Ziegler, the decomposition of the iron nitride layers upon heating was studied in an atmosphere of ammonia, although one experiment was made in air and in this the decomposition appeared to be greater. The fact that the iron-nitrogen system should not be considered as a stable system but as a metastable one was emphasized in the paper. No tests were made of the decomposition of the iron-nitrogen alloys in vacuum.

Mr. Kinzel's statement that by the use of a new etching reagent which Mr. Vilella has developed, three layers are brought out in the aluminum type steel after nitriding, is very interesting indeed. With the ordinary etching reagents such as 5 per cent picric acid in alcohol and hot alkaline sodium picrate only one layer was revealed in the nitriding steels described in the paper, even after very deep etching.

I was very glad to get Mr. Merten's comments but it seems to me that perhaps the opposite view is the better one. He asks why we should concern ourselves here with the compounds of the pure iron-nitrogen system when we know that in practical nitriding only the complex alloy nitriding steels can be used. On the other hand, I get the impression from the papers and discussion at this symposium that what we have in respect to the complex nitriding steels is a lot of more or less unrelated data and information, but what we lack is a better understanding of the underlying principles. It is only natural that we should all rush in and try to gather as much information as we can on this new process. It is quite possible, however, that we would make even faster progress if we stopped to make a fundamental study, first of the constitutional diagram of the iron-nitrogen system, and then of the diagram of the more complex nitriding steels.

A STUDY OF THE NITRIDING PROCESS—PART I*

By V. O. Homerberg and J. P. Walsted

Abstract

A study of some of the factors involved in the nitriding process are considered. The necessary equipment and the method of performing the nitriding operation are described. The physical properties of the nitriding steels in the heat treated but un-nitrided condition and the physical properties of these steels in the nitrided state at ordinary and at elevated temperatures are given.

The results of a microscopic study of nitrided specimens reheated at 100-degree Fahr. intervals between 1000 and 2000 degrees Fahr. (540-1095 degrees Cent.), inclusive, followed by furnace cooling and water quenching, indicate that no appreciable change in microstructure occurs until a temperature of 1400 degrees Fahr. (760 degrees Cent.) is attained. Photomicrographs are included to show the changes in microstructure.

Specimens nitrided at 100-degree intervals from 800 to 1400 degrees Fahr. (425-760 degrees Cent.), inclusive, show increased depth of case with increase in temperature from 800 to 1300 degrees Fahr. (425-705 degrees Cent.), but a decrease in hardness with increase in temperature.

It has been found that the present nitriding steels are not subject to temper brittleness. The hardness and the shock resisting properties of the core are not influenced by the nitriding of properly heat treated parts.

The question of protection against nitriding has been investigated with positive results. Although nickel plating or a coating of tin or solder is generally recommended, a suspension of stannous or stannic oxide in a suitable vehicle is easy to apply and gives satisfactory results.

Parts to be nitrided must be free from decarburization to prevent spalling of the case. Strains must be completely eliminated by suitable heat treatment before

*This paper represents portions of a thesis presented by J. P. Walsted to the Massachusetts Institute of Technology as partial fulfillment for the degree of Doctor of Science in Metallurgy.

Of the authors, members of the society, V. O. Homerberg is associate professor of physical metallurgy at the Massachusetts Institute of Technology, and consulting metallurgist to the Ludlum Steel Company; J. P. Walsted is instructor in physical metallurgy at the Massachusetts Institute of Technology. Manuscript received June 5, 1929.

nitriding in order to prevent warping or distortion in the finished articles.

The growth of parts during the nitriding operation has been measured and attention is called to the augmented growth that takes place at sharp corners.

Introduction

THE growing interest manifested in the case hardening of special steels with ammonia gas to obtain extraordinary surface hardness without warping or distortion indicates that the evolution of these special steels, together with the ammonia case hardening process, represents one of the most important metallurgical developments in recent years.

The ammonia case hardening process, which is termed "nitriding", consists in subjecting the machined and preferably heat-treated articles to the action of ammonia gas under certain conditions whereby remarkable surface hardness is imparted to the material without any further treatment. Remarkable wear-resisting properties together with retention of hardness at elevated temperatures and marked resistance to atmospheric, water and salt water corrosion are obtained by this method.

The common method of case hardening involves a heat treatment after the carburization of the material. Articles treated under these conditions undergo warping or distortion and possess far less surface hardness than that obtained by nitriding.

Although the introduction of nitrogen into steel through the medium of ammonia gas is not new, credit for the present practicability of the process is due to the thorough study of the problem by Dr. Adolph Fry of the Krupp Works in Essen, Germany, and to its further development by investigators in this country and abroad. The evolution of the steels containing aluminum represented the most important factor in eliminating the difficulties formerly experienced in attempting to nitride satisfactorily the steels which were available before the publication of the results obtained by Dr. Fry.

In any process so newly developed, it is obvious that many factors arise which must be investigated in order to adapt it successfully to commercial applications. A study of the conditions of time, temperature, dissociation of ammonia, together with the

question of the condition of the steel before case hardening with ammonia, as well as the means of protection of certain parts against nitriding is of great importance industrially.

The complete study of the nitriding process is too great and too broad for any one investigator. For this reason, this research has been limited to a few outstanding phases of the problem. Some of them have been completed at the present time while others are nearing completion and will be presented at a later time.

The phases of the problem which are included in this paper are:

1. The influence of time of nitriding on the depth of case obtained.
2. The influence of temperature on the depth and hardness of the case obtained.
3. The effect of the amount of dissociation of the ammonia on the character of the case.
4. The means of protection against nitriding.
5. The influence of the surface condition of the steel, such as the presence of decarburization, on nitriding.
6. The influence of materials added to the ammonia, such as water vapor and organic nitrogenous compounds.

Further studies, which are nearing completion and will be discussed in later papers, include:

1. X-ray studies to determine the mode of nitrogen absorption and to explain some of the phenomena which have been observed microscopically.
2. The effect of pressure on the nitriding operation.
3. Wear tests conducted at temperatures ranging from room temperature to 1000 degrees Fahr. (540 degrees Cent.).
4. A thorough study of the resistance of nitrided material to various corrosive media.
5. A study of the use of nitriding agents other than ammonia.
6. The development of materials other than steel that can be surface hardened with ammonia.
7. A study of the nitrided structure at high magnifications.
8. A study of the use of catalytic agents in nitriding.
9. A study of the role played by hydrogen during the nitriding operation.

Review of the Literature

Sawyer[1] has presented such an excellent review of the literature concerning the reactions and effects of nitrogen on steel that further mention of the work of various investigators will be given only in instances where results have been reported since the publication of his article and in cases where it may seem directly pertinent to the particular phase of the subject under discussion.

Physical Properties of Chromium-aluminum Nitriding Steels

It has been stated previously that the evolution of the present series of alloy steels containing aluminum has made possible the present commercial success of the ammonia case hardening process. The thorough study of the problem by Dr. Fry[2] began with the determination of the combining power of various alloying elements toward nitrogen and the stability of the resulting nitrides. He found that aluminum ranked first, both as to the amount of nitrogen with which it combined as well as the stability of the aluminum nitride formed. This compound showed no loss in nitrogen even when heated at 1832 degrees Fahr. (1000 degrees Cent.). Other elements which formed nitrides with high nitrogen contents include molybdenum, manganese, chromium, vanadium, titanium and tungsten in the order named.

Dr. Fry determined next the extent of the surface hardening effect by ammonia on plain carbon steels, various alloy steels and finally on special alloy steels containing aluminum, and aluminum together with other alloying elements, such as chromium and molybdenum. The outcome of this investigation was the manufacture of a series of alloy steels containing varying amounts of carbon, together with approximately 1.25 per cent aluminum, 1.5 per cent chromium and 0.2 per cent molybdenum.

Alloy steels having this particular combination of alloying elements were chosen because they showed the maximum surface hardness when exposed to ammonia gas under definite conditions. Furthermore, this hardness was retained at elevated temperatures and

[1] C. B. Sawyer, "Reactions and Effects of Nitrogen on Steel—A Supplementary Review of Literature", Transactions, American Society for Steel Treating, Vol. 8, September, 1925, p. 291.

[2] A. Fry, "Stickstoff in Eisen, Stahl und Sonderstahl. Ein Neues Oberflaechenhaertungsverfahren", *Stahl und Eisen*, Vol. 43, 1923, p. 1271.

the specimens showed a marked resistance to atmospheric, water and salt water corrosion.†

The results obtained by nitriding chromium-vanadium steels containing a minimum of 0.4 per cent vanadium have been reported by Kinzel[3] and the nitriding of aluminum-molybdenum steels has been considered by McQuaid and Ketcham.[4]

Mr. Zavarine[5] and one of the present authors determined the physical properties of several aluminum-chromium steels without molybdenum, one of which contained nickel. The addition of molybdenum was made later in order to increase the toughness of the core and the case and to eliminate the possibility of "Krupp sickness" in the steel after slow cooling from the nitriding temperature. The impact values of these steels both with and without molybdenum and after nitriding for various lengths of time will be considered later in the discussion of the properties of nitrided steels.

The analyses of the steels considered in this investigation are given in Table I. The physical properties of three of the steels after proper heat treatment and before nitriding are given in Tables II, III and IV. Particular attention is called to the high impact values which indicate that these steels have high shock-resisting properties.

Heat treating by quenching, followed by drawing or tempering at a temperature not lower than 1000 degrees Fahr. (540 degrees Cent.), in order to obtain a fine sorbitic structure before nitriding, is important. McQuaid,[6] in a recent paper, stresses this point.

Since the temperature used in nitriding to obtain maximum hardness for the case is approximately 950 degrees Fahr. (510 degrees Cent.), it will be noted from Table II that the physical properties of the core after a temper at 1000 degrees Fahr. (540 degrees Cent.) are high, although a long exposure at 950 degrees

†These steels are marketed under the name of "Nitralloy", the different ranges of carbon content being designated as grades "G", "H", etc.

[3]A. B. Kinzel, "Steels for Case Nitrification", TRANSACTIONS, American Society for Steel Treating, Vol. 14, August, 1928, p. 248.

[4]H. W. McQuaid and W. J. Ketcham, "Some Practical Aspects of the Nitriding Process", TRANSACTIONS, American Society for Steel Treating, Vol. 14, November, 1928, p. 719.

[5]V. O. Homerberg and I. N. Zavarine, "Physical Properties of Several Chromium-aluminum and Chromium-nickel-aluminum Steels", TRANSACTIONS, American Society for Steel Treating, Vol. 13, February, 1928, p. 297.

[6]H. W. McQuaid, "Working Rules for Nitrogen Hardening", *Iron Age*, Vol. 123, May 9, 1929, p. 1272.

Table I
Chemical Analysis of Steels Studied

	"G"	"H"	"I"
Carbon	0.36	0.23	0.16
Manganese	0.51	0.51	0.55
Silicon	0.27	0.20	0.46
Aluminum	1.23	1.24	0.88
Chromium	1.49	1.58	1.70
Nickel	0.48	0.57	0.53
Molybdenum	0.18	0.20	0.21
Sulphur	0.010	0.011	0.010
Phosphorus	0.013	0.011	0.018

Table II
Physical Properties of Grade "G" Steel
Previously Oil-quenched from 1650 Degrees Fahr. (900 Degrees Cent.)

Tempering Temperature Deg. Fahr. Deg. Cent.	Yield Point	Maximum Strength	Elong. in 2 inches	Red. of Area	Charpy ft. lbs.	Brinell Hardness
800 425	180,000	224,500	11	36	12.0	445
900 480	165,000	206,300	11.5	37.5	15.0	415
1000 540	158,500	182,500	15	50	22.0	363
1100 590	137,500	156,000	16.5	57	35.2	330
1200 650	120,000	138,000	20	60	44.0	285
1300 705	103,300	121,000	23	62.5	55.3	226
1400 760	80,500	104,300	28	59	54.5	200
Annealed	69,000	95,000	30	67.5	31.6	186

Table III
Physical Properties of Grade "H" Steel
Previously Oil-quenched from 1750 Degrees Fahr. (955 Degrees Cent.)

Tempering Temperature Deg. Fahr. Deg. Cent.	Yield Point	Maximum Strength	Elong. in 2 inches	Red. of Area	Charpy ft. lbs.	Brinell Hardness
800 425	156,200	178,800	12	47	20.6	400
900 480	143,500	170,000	16	49	25.5	365
1000 540	133,300	160,000	17	54	30.1	340
1100 590	117,500	134,500	18	61	48.1	290
1200 650	103,800	122,000	21.5	67	59.2	255
1300 705	85,500	102,500	27	72	69.0	228
1400 760	75,000	90,500	32	73	73.0	190
Annealed	60,000	80,000	34	70.5	47.8	157

Fahr. (510 degrees Cent.) during the nitriding operation may alter these properties somewhat. Additional reasons for advocating the nitriding of heat treated articles will be considered later.

Table IV
Physical Properties of Grade "I" Steel

Previously Oil-quenched from 1750 Degrees Fahr. (955 Degrees Cent.)

Tempering Temperature Deg. Fahr. Deg. Cent.	Yield Point	Maximum Strength	Elong. in 2 inches	Red. of Area	Charpy ft. lbs.	Brinell Hardness
800 425	133,750	159,500	15.5	60.3	36.0	336
900 480	127,500	154,750	16.8	58.2	39.1	331
1000 540	126,500	148,000	16.2	61.0	44.9	321
1100 590	112,500	126,500	18.0	66.9	60.2	285
1200 650	100,000	113,500	22.0	71.0	65.3	232
1300 705	79,500	96,750	27.3	75.0	81.5	202
1400 760	67,750	85,500	32.5	75.0	90.5	170
Annealed	47,750	78,250	34.5	67.1	....	134

The Nitriding Process

The Fry process for case hardening with ammonia offers many decided advantages in that all of the heat treating of the articles is done before the nitriding and no further treatment is necessary after their exposure to the ammonia gas. The temperature used is so low that no appreciable warping or distortion will take place provided that all of the strains produced in machining and in hardening have been removed. The articles to be case hardened should be machined and heat treated to give the desired physical properties to the core. All traces of decarburization and all strains must be eliminated before the subjection of the articles to the ammonia treatment.

The equipment required for the case hardening of articles with ammonia consists of a suitable furnace provided with automatic temperature control, a gas-tight container made of a material such as chrome-iron, which will not be acted upon when exposed to ammonia at the nitriding temperature, a tank of ammonia provided with a suitable needle valve for controlling the flow of the gas, inlet and outlet tubes, and finally, a special pipette for determining the extent of the ammonia dissociation.

Fig. 1 gives a schematic outline of the required apparatus. The tank of ammonia must be placed in a position such that the bent tube inside of the tank has its open end in the gaseous atmosphere and does not dip into the liquid ammonia.

A suitable needle valve, together with a pressure gage, insures the control of a steady and even flow of the gas. The inlet and outlet tubes are made of nickel and the articles in the box are

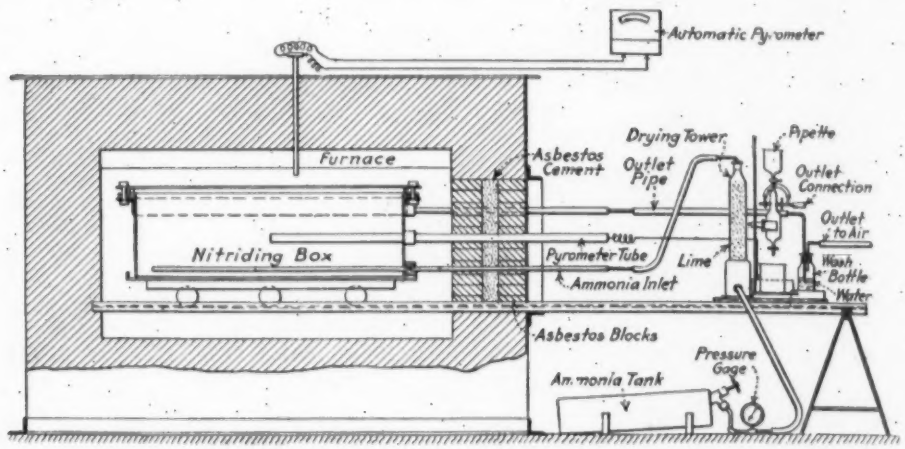


Fig. 1—A Schematic Outline of the Apparatus Required for Hardening with Ammonia Gas.

supported on nickel gauze. The inlet tube extends along the bottom of the box to the back, while the outlet tube is at the front end and near the top of the box. Pyrometers are inserted into both the container and the furnace. The furnace pyrometer is connected to the automatic control. The gas mixture from the container passes through a wash bottle to indicate the gas pressure, which is generally ½ to 1 inch of water, as well as the rate of flow of the gas, and finally passes into the atmosphere or is washed into the drain in the sink by means of a suitable baffle.

The ammonia gas decomposes to a certain extent into nitrogen and hydrogen according to the following reaction:

$$2NH_3 \rightleftarrows 2N + 3H_2$$

The nitrogen, which is very active at the moment of decomposition of the ammonia gas, undoubtedly combines to a certain extent with the iron and with the alloying elements in the steel to form nitrides. These nitrides, which are in solid solution or, more likely, in a fine state of dispersion in the case, impart extreme hardness to the

surface of the steel, a hardness which gradually decreases inwardly until it corresponds to that of the core.

The gas mixture leaving the furnace consists of hydrogen, nitrogen and undissociated ammonia. The ammonia gas is very soluble in water, whereas the hydrogen and the nitrogen are in-

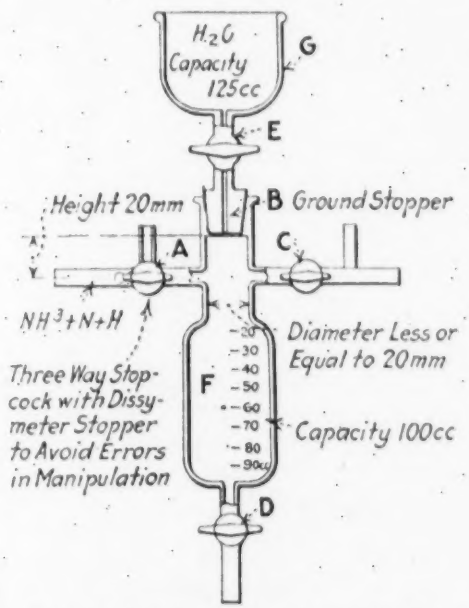


Fig. 2—Details of the Pipette Used for Determining the Extent of the Ammonia Dissociation.

soluble. Advantage is taken of this fact in the determination of the extent of the ammonia dissociation during the nitriding operation. The special pipette is used for making this determination.

The pipette used for determining the extent of the ammonia dissociation is shown in Fig. 2. It has a three-way stopcock at point "A" and two-way stopcocks at points "C," "D" and "E." The purpose of the three-way stopcock is to by-pass the gas mixture while a determination is being made. In order to make this determination, the gas is allowed to fill chamber "F" while "C" is closed. The chamber "G" is filled with water. Stopcock "D" is closed and then the gas is by-passed by means of stopcock "A". The chamber "F" is now filled with a mixture of hydrogen, nitrogen and undissociated ammonia. The stopcock "E" is opened, whereby the water runs into the gas-filled chamber. The undissociated ammonia is absorbed immediately. The gas mixture above the water solution represents the mixture of hydrogen and nitrogen.

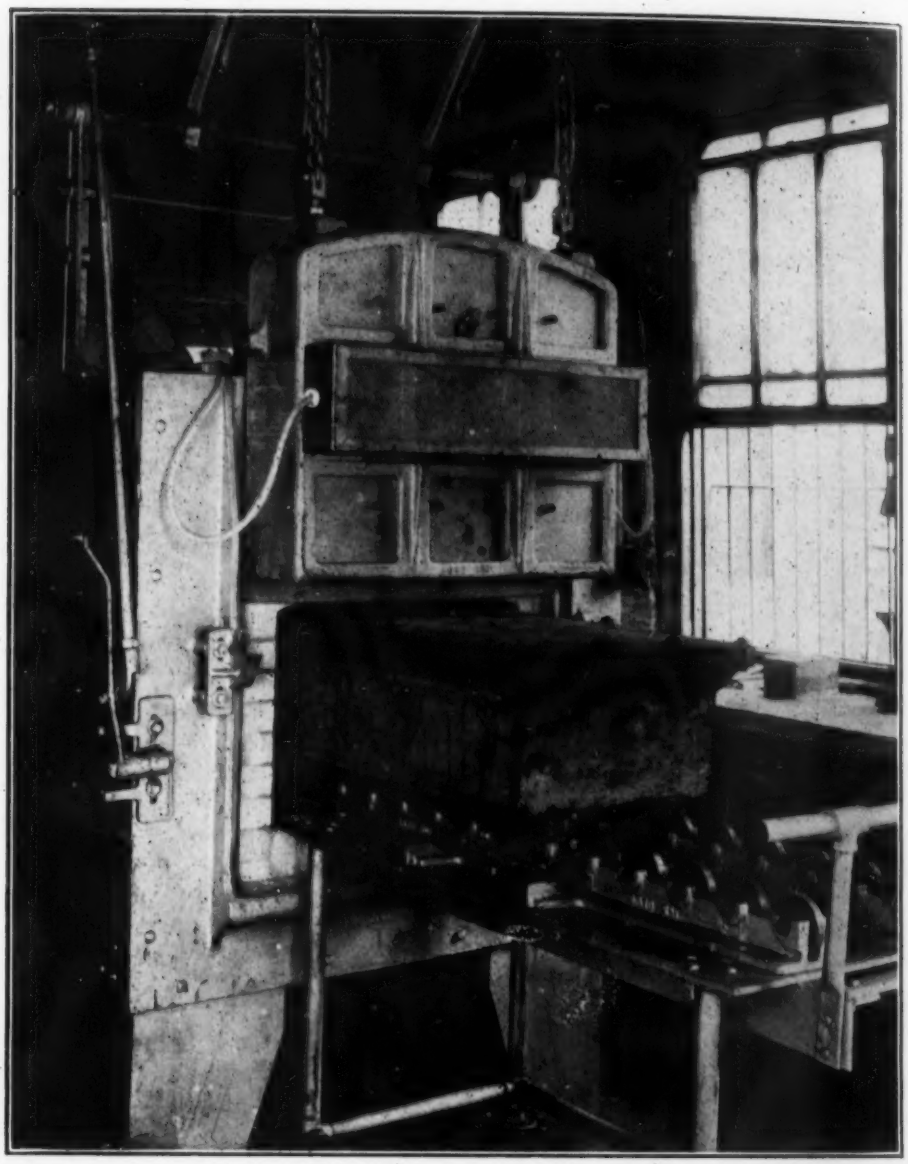


Fig. 3—Showing How Box is Placed in the Electric Furnace.

The scale on chamber "F" reads directly in per cent of dissociation. If the water solution reaches the 30 per cent mark, it means that 30 per cent of the ammonia has dissociated. If the reading is higher than this value the gas flow should be increased by means of the needle valve, while if the reading is lower than 30 per cent, the gas flow should be decreased, since 30 per cent is the most desirable value, although a range of 20 to 40 per cent is satisfactory

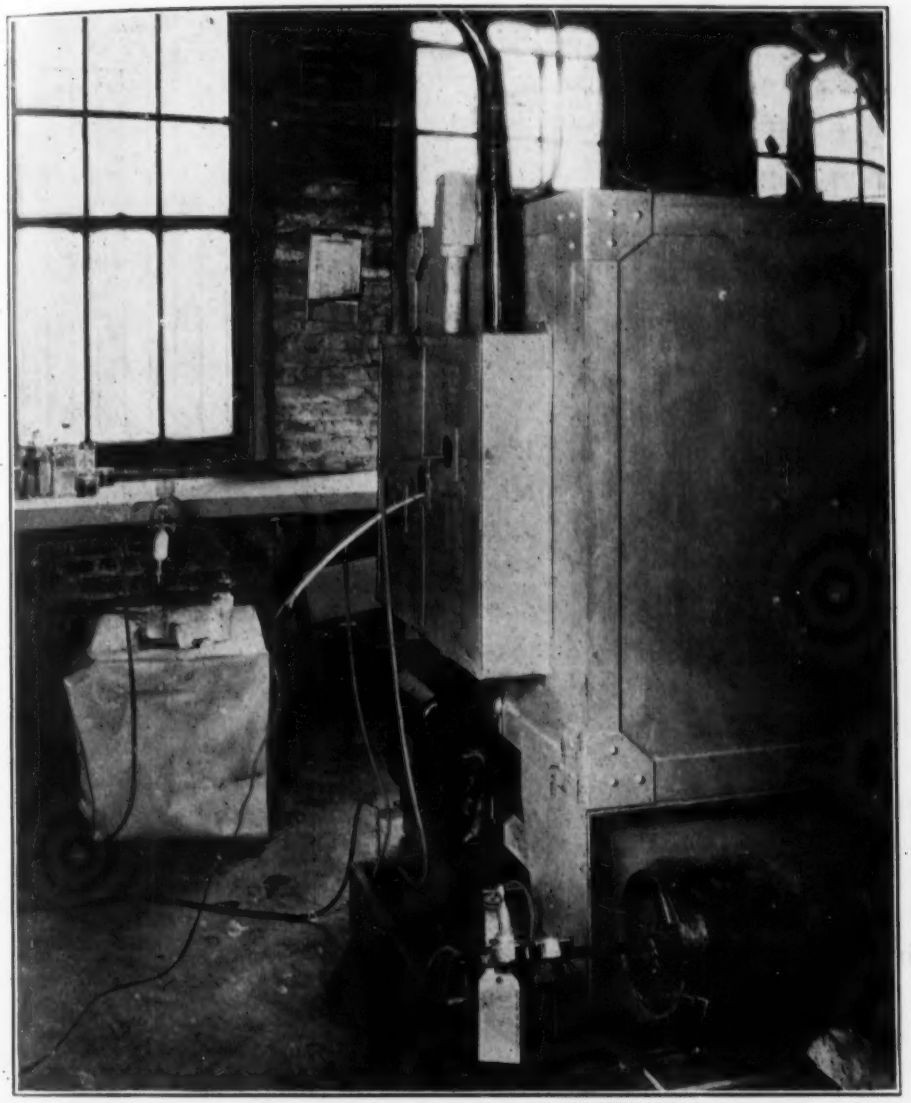


Fig. 4—Back of the Electric Furnace and the Tank Connection. The Pipette is Shown Below in Background.

when the nitriding temperature range is 900 to 1000 degrees Fahr.

Figs. 3 and 4 show the front and back views of a commercial installation. Fig. 3 also shows the box for holding the articles to be nitrided. The cover is bolted to the flange of the box and is kept gas-tight by employing a suitable gasket. Asbestos washers or asbestos packing, preferably covered with aluminum foil, are generally used as a seal. Merten[7] uses nickel wire as a seal and

[7]W. J. Merten, "The Process of Surface Hardening of Steel by Nitriding". *Fuels and Furnaces*, Vol. 6, October, 1928, p. 1371.

employs clamps with suitable wedges for making the container gas-tight. The furnace is provided with rollers, which should extend in front of the furnace to facilitate the withdrawal of the box

Table V
Physical Properties of Nitrided Steel "G"

Oil-quenched from 1650 degrees Fahr. (900 degrees Cent.).
Tempered at Indicated Temperature.
Nitrided 90 hours at 900 degrees Fahr. (480 degrees Cent.), slowly cooled.

Tempering Temperature, Degrees Fahr. Degrees Cent.	Yield Point, lbs. per sq. in.	Maximum Strength, lbs. per sq. in.	Elongation in 2 inches, per cent	Reduction of area, per cent	Charpy ft. lbs.
1000 540	139,000	171,300	6.0	13.0	13.5
1100 590	128,500	158,800	5.0	16.0	18.2
1200 650	110,000	137,800	4.0	17.0	20.7
1300 705	97,500	122,800	8.0	20.5	23.5
1400 760	82,500	109,500	7.5	17.0	23.9
Annealed	63,500	101,800	8.5	14.0	11.4

for charging. Fig. 4 indicates the positions of the inlet and outlet tubes as well as that of the pyrometer. It also shows the tank connection and the pipette.

A recent and a very promising development in a nitriding furnace makes use of a fan to effect gas circulation. This furnace has a door to facilitate the charging and the discharging of the racks containing the articles to be nitrided. Bolts and packing for sealing have been eliminated, excellent results have been reported by a number of industrial users of this type of furnace.

Influence of Nitriding on Physical Properties

Standard tensile specimens of steel "G" were used in determining the effect of nitriding on the physical properties. The specimens were oil-quenched from 1650 degrees Fahr. (900 degrees Cent.), followed by a temper for 1 hour at 100-degree Fahr. intervals from 1000 to 1400 degrees Fahr. (540 to 760 degrees Cent.), inclusive. The specimens were then nitrided for 90 hours at 900 degrees Fahr. (480 degrees Cent.) and cooled slowly in a stream of ammonia. The results of the tests are given in Table V. Two specimens were broken in each instance. That the resistance to impact should be appreciably reduced by nitriding is to be expected. In spite of this fact, however, the Charpy values are very satisfactory.

Standard 0.505 test specimens of steel "G" were tested in tension at temperatures ranging from 800 to 1400 degrees Fahr. (425 to 760 degrees Cent.), in order to determine the suitability of this nitrided steel for use at high temperatures for short periods of time. The specimens were oil-quenched from 1650 degrees Fahr. (900 degrees Cent.), after holding at temperature for a half hour. They were then tempered at 1000 degrees Fahr. (540 degrees Cent.) for 1 hour.

The heat treated specimens were nitrided at 900 degrees Fahr. 1480 degrees Cent.) for 90 hours, then tested at elevated temperatures. The character of some of the failures made it impossible to procure accurate values for elongation and reduction of area. These values have been omitted in such instances.

Table VI gives the results of the high temperature tests. No experiments have been performed to obtain data on the physical properties of these nitrided steels at elevated temperatures over long periods of time.

Table VI

Steel "G", Previously Oil-quenched from 1650 Degrees Fahr. (900 Degrees Cent.) and Tempered at 1000 Degrees Fahr. (540 Degrees Cent.), followed by Nitriding for 90 Hours at 900 Degrees Fahr. (480 Degrees Cent.)

Testing Temperature, Degrees Fahr. Degrees Cent.	Maximum Strength, pounds per square inch	Elongation in 2 inches, per cent	Reduction of Area, per cent
800 425	133,800	6.5	30.5
900 480	124,300	9.5	31.0
1000 540	98,000	15.5	44.5
1100 590	41,750	....	....
1200 650	39,000	....	....
1300 705	27,600	....	....
1400 760	19,550	....	....

Properties of the Core of Nitrided Steels

It has been known for many years that certain steels, particularly those of the chromium-nickel type, are subject to temper brittleness. This phenomenon, sometimes known as "Krupp sickness," is shown by a marked decrease in resistance to impact when the previously hardened steels are slowly cooled from a tempering temperature, generally between 750 and 1200 degrees Fahr. (400 and

650 degrees Cent.). This brittleness may be eliminated by quenching from the tempering temperature.

The earlier nitriding steels contained chromium and nickel in quantities large enough to put them in the class of steels subject to "Krupp sickness". The present steels contain molybdenum instead of nickel.

Guillet[8] has found that chromium-aluminum-nickel steels are susceptible to "Krupp sickness" and that the addition of molybdenum corrects this disadvantage.

The nitriding process involves slow cooling from a temperature within the range which causes temper brittleness. It seemed advisable, therefore, to make a thorough investigation of this problem. The analyses of the steels which were used in the present investigation are given in Table VII.

Table VII

Analysis of Steels Used in This Investigation

Steel No.	5702	5181	D7B	D7D
C	0.46	0.31	0.25	0.31
Mn	0.54	0.64	0.56	0.56
Si	0.37	0.75	0.33	0.18
Cr	1.80	1.40	1.65	1.43
Al	1.15	1.04	1.11	1.30
S	below 0.02	below 0.02	0.015	0.020
P	below 0.02	below 0.02	0.016	0.018
Mo	0	0	0	0.18
Ni	0	1.83	0	0

Four Charpy specimens were made from each of the steels. These specimens were oil-quenched from 1650 degrees Fahr. (900 degrees Cent.) and tempered at 1000 degrees Fahr. (540 degrees Cent.) for 2 hours. Specimens Nos. 1 and 2 were quenched from the tempering temperature, while Nos. 3 and 4 were slowly cooled.

In order to determine the influence of nitriding on the resistance to shock, regular Charpy specimens, heat treated in the same manner as 3 and 4, were nitrided for 24, 48 and 72 hours at 950 degrees Fahr. (510 degrees Cent.). These specimens give the total effect of nitriding on the impact properties. As the influence of nitriding on the core is of importance, samples were made which were 0.060 inch oversize. These samples were heat treated in the same manner as samples 3 and 4 and then nitrided for 24, 48 and

[8]Leon Guillet, "La Nitruration des Aciers et son Utilisation Industrielle", *Le Genie Civil*, Vol. 91, 1927, pp. 36, 60, 86, 472.

72 hours at 950 degrees Fahr. (510 degrees Cent.). After nitriding, they were reduced by grinding to regular Charpy size and tested. The removal of 0.030 inch from each side was sufficient to eliminate all of the case.

These specimens show the effect of nitriding on the core of the steel. In order to separate the effect of the nitriding from the effect of holding the specimens at the nitriding temperature for long periods of time, additional oversize specimens were prepared which were treated in the same manner except that they were protected against the action of ammonia by a coating of tin. By protecting the samples in this manner no nitriding takes place and the influence of the furnace temperature on the steel is determined.

The schedule of operations in this investigation was as follows:

Samples 1 and 2—Regular Charpy specimens, quenched from the drawing temperature. Not nitrided.

Samples 3 and 4—Regular Charpy specimens. Slowly cooled from the drawing temperature. Not nitrided.

Samples 5 and 6—Regular Charpy specimens. Heat treated. Nitrided at 950 degrees Fahr. (510 degrees Cent.) for 24 hours.

Samples 7 and 8—Regular Charpy specimens. Heat treated. Nitrided at 950 degrees Fahr. for 48 hours.

Samples 9 and 10—Regular Charpy specimens. Heat treated. Nitrided at 950 degrees Fahr. for 72 hours.

Samples 11 and 12—Oversize Charpy specimens. Heat treated. Nitrided at 950 degrees Fahr. for 24 hours. Case removed and specimens reduced to regular Charpy size.

Samples 13 and 14—Oversize Charpy specimens. Heat treated. Nitrided at 950 degrees Fahr. for 48 hours. Case removed and specimens reduced to regular Charpy size.

Samples 15 and 16—Oversize Charpy specimens. Heat treated. Nitrided at 950 degrees Fahr. for 72 hours. Case removed and specimens reduced to regular Charpy size.

Samples 17 and 18—Oversize Charpy specimens. Heat treated. Tinned to prevent nitriding. Nitrided at 950 degrees Fahr. for 24 hours. Specimens reduced to regular Charpy size.

Samples 19 and 20—Oversize Charpy specimens. Heat treated. Tinned to prevent nitriding. Nitrided at 950 degrees Fahr. for 48 hours. Specimens reduced to regular Charpy size.

Samples 21 and 22—Oversize Charpy specimens. Heat treated. Tinned to prevent nitriding. Nitrided at 950 degrees Fahr. for 72 hours. Specimens reduced to regular Charpy size.

The results of the impact and hardness tests are given in Table VIII.

Table VIII
Impact and Hardness Tests

Steel Number	5702		5181		D7B		D7D	
Specimen Number	Charpy ft. lbs.	Rockwell Hardness "C" scale	Charpy ft. lbs.	Rockwell Hardness "C" scale	Charpy ft. lbs.	Rockwell Hardness "C" scale	Charpy ft. lbs.	Rockwell Hardness "C" scale
1 and 2 average	12.5	35	15.5	32	33	23	33	31
3 and 4 average	12	36	14.5	32	32	22	33.5	32
5 and 6 average	6.5	..	6.5	..	20	..	22	..
7 and 8 average	3	..	4.5	..	15.5	..	19	..
9 and 10 average	3.5	..	2	..	11.5	..	15.5	..
11 and 12 average	7.5	37	7.5	34	31	22	33	32
13 and 14 average	4.5	36	6.5	35	28.5	21	32	31
15 and 16 average	7	35	7	34	27	22	35	32
17 and 18 average	8	33	8	32	30.5	24	37.5	30
19 and 20 average	5	32	7	35	25	24	30	31
21 and 22 average	6.5	32	6.5	33	24.5	24	34	31

A study of Table VIII shows that there is no temper brittleness in any of the steels investigated. The close agreement between the values obtained on testing specimens 1, 2, 3 and 4 indicate that the impact resistance and hardness are the same whether the steel is slowly cooled or quenched from the drawing temperature.

The results obtained by testing the nitrided regular Charpy samples 5 to 10, inclusive, show that increasing the nitriding time reduces the impact value. This is to be expected, as the case has relatively little shock resistance. The presence of the nitride case amounts to a reduction of the cross sectional area of the specimen. The thicker case produced by the longer nitriding time leaves less of the core material to resist impact and so reduce the Charpy values obtained. The nitrided oversize specimens, 11 to 16, inclusive, show fairly close agreement in impact values as well as hardness. It is evident that nitriding has little, if any, influence on these properties of "D7D" containing molybdenum, but no nickel. The impact resistance of the core of D7B has evidently been reduced somewhat by the nitriding treatment. This reduction, however, is

due to the nitriding temperature, rather than to any action of ammonia, as can be seen by referring to the values obtained on samples 17 to 22, inclusive. Steels 5702 and 5181 also show an appreciable reduction of shock resisting properties of the core. Again referring to samples 17 to 22 of these steels it is seen that the reduction of impact resistance is due to the exposure of the specimens for a long time to the furnace temperature, rather than to the action of ammonia. The hardness values in all cases are in fairly close agreement with those obtained on the heat treated un-nitrided samples.

From the foregoing experiment it is seen that nitriding has little or no influence on the hardness and impact properties of the core of nitrided steels. However, holding the samples at the nitriding temperature reduces materially the impact properties of steels 5702 and 5181 and to a less degree D7B. Steel D7D, containing chromium, aluminum and molybdenum, shows no reduction in impact resistance of the core, due to the action of ammonia or to the furnace temperature. Steels 5702 and 5181 show about the same reduction in the impact properties of the core. It is evident from this that the high nickel content of 5181 is not the cause of this steel becoming somewhat brittle when held for a long time at 950 degrees Fahr. (510 degrees Cent.).

That molybdenum is a valuable alloying element in steels used for nitriding is evident. The retention of the shock resisting properties of the core of nitriding steels, containing this element, if subjected to the nitriding process is of great value. In view of the fact that the case depths obtained when this steel was nitrided for 24, 48 and 72 hours, were 0.011 inch, 0.017 inch and 0.024 inch respectively, the Charpy values obtained are very high.

The present series of steels, of which D7D is a typical sample, all contain molybdenum as an alloying element.

Temperature and Time of Nitriding

Machlet[9] of the American Gas Company obtained a patent in 1913 for nitriding steel and cast iron above 900 degrees Fahr. (480 degrees Cent.). The materials available at that time were of such a character that the case obtained on exposure to ammonia gas,

[9]Adolph Machlet, U. S. Patent. June 24, 1913.

although very hard, was superficial and, therefore, found only a limited application.

The evolution by Dr. Fry of alloy steels containing aluminum changed greatly certain characteristics of the nitrided case, especially the depth, after exposing these steels to the action of ammonia gas at relatively low temperatures.

Fry recommends that the nitriding should be done at a temperature below the eutectoid temperature in order to eliminate

Table IX
Nitriding Steels "H" and "I"

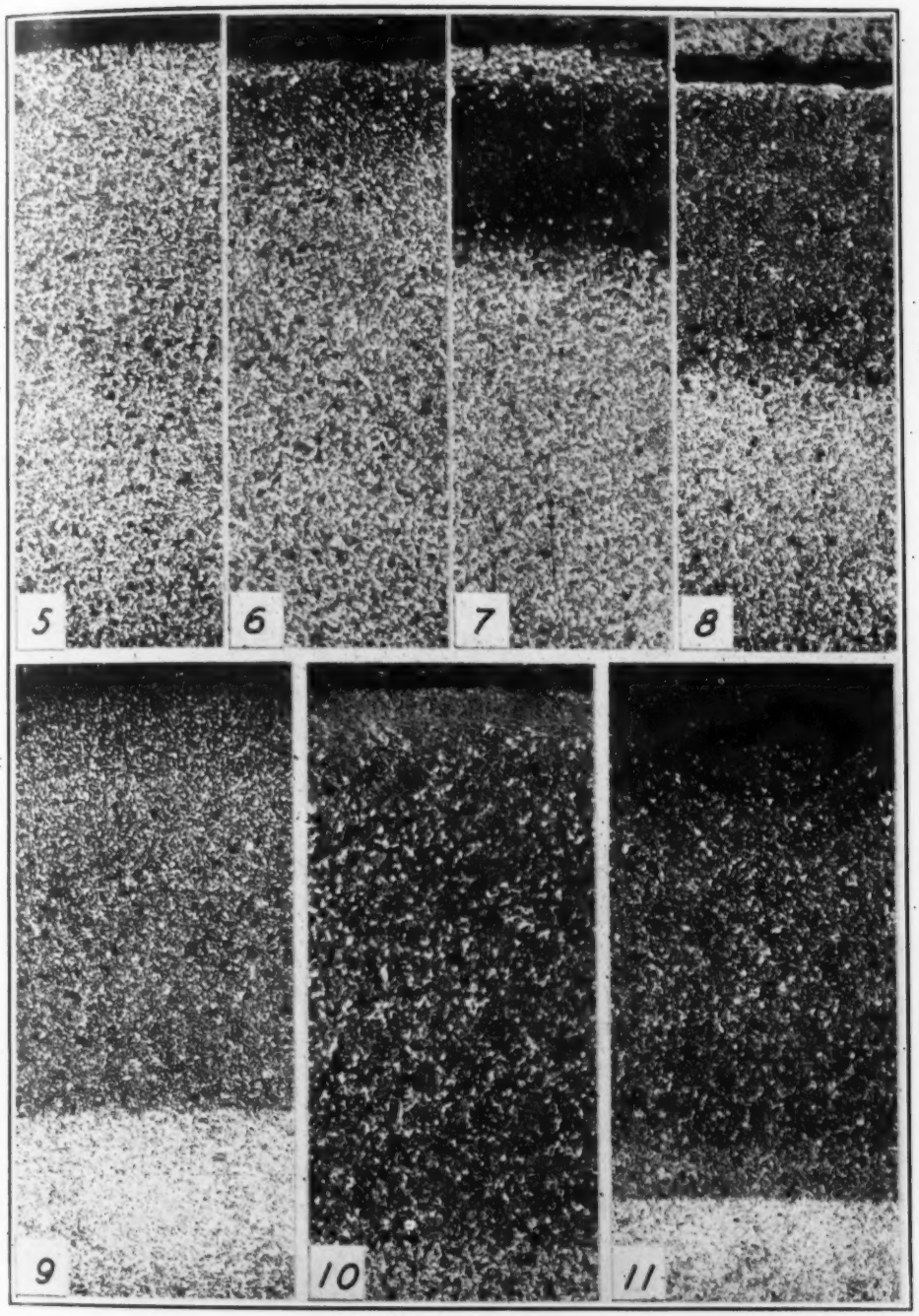
Nitriding Temperature Degrees Fahr. Degrees Cent.	Nitrided 48 Hours at Indicated Temperature. Depth of Case in Inches "H"	"I"	Brinell Hardness "H"	"I"
800 425	Trace	Trace	700	800
900 480	0.010	0.012	1140	1160
1000 540	0.020	0.025	990	960
1100 590	0.028	0.030	905	840
1200 650	0.040	0.045	780	765
1300 705	0.051	0.057	685	670
1400 760	0.047	0.050	670	670

warping or distortion and the possible formation of brittle layers. It is obvious that this temperature will vary with the character of the steel.

The nitriding operation in commercial practice is conducted at temperatures ranging from 900 to 1000 degrees Fahr., 950 degrees Fahr. being the most common. In order to determine the depth and hardness of the case obtainable by exposure to ammonia gas at higher temperatures, specimens of steels "H" and "I" were nitrided for 48 hours at temperatures ranging from 800 to 1400 degrees Fahr. (425 to 760 degrees Cent.), inclusive. The hardness values were determined with a Herbert pendulum and converted into Brinell units.

The results of the experiment are given in Table IX. The values for depth of case obtained in industrial nitriding furnaces are generally greater than those indicated in this table.

On nitriding steels "H" and "I" at 800 degrees Fahr. (425 degrees Cent.) the surface was found to be hard when tested with



Figs. 5 to 11—Photomicrographs of Steel "H" Nitrided 48 Hours at 800 to 1400 Degrees Fahr., Respectively. Dissociation for Figs. 5 to 8 was 30 per cent. Figs. 9, 10 and 11 were 50, 85 and 95 per cent respectively. Nital Etch. × 50.

a file, showing that at this low temperature an appreciable amount of nitrogen had been absorbed. On microscopic examination, how-

ever, only slight evidence of a case could be detected. A photomicrograph of the steel "H" specimen is shown in Fig. 5. There is a definite case formation above 800 degrees Fahr., as shown by the values in Table IX and in the photomicrographs in Figs. 6 to 11, inclusive. An interesting feature of the values obtained for the various temperatures is the falling off in the depth of case when nitrided at 1400 degrees Fahr. (760 degrees Cent.). The ammonia dissociation was kept at 30 per cent until 1200 degrees Fahr. (650 degrees Cent.) was reached. At this temperature and above, this value was exceeded. At 1200, 1300 and 1400 degrees Fahr. (650, 705 and 760 degrees Cent.) the dissociation values were 50 per cent, 85 per cent and 95 per cent in the order given. The degree of dissociation increases rapidly with the temperature and it was found impractical to keep it at 20-40 per cent by greatly increasing the flow of the ammonia gas.

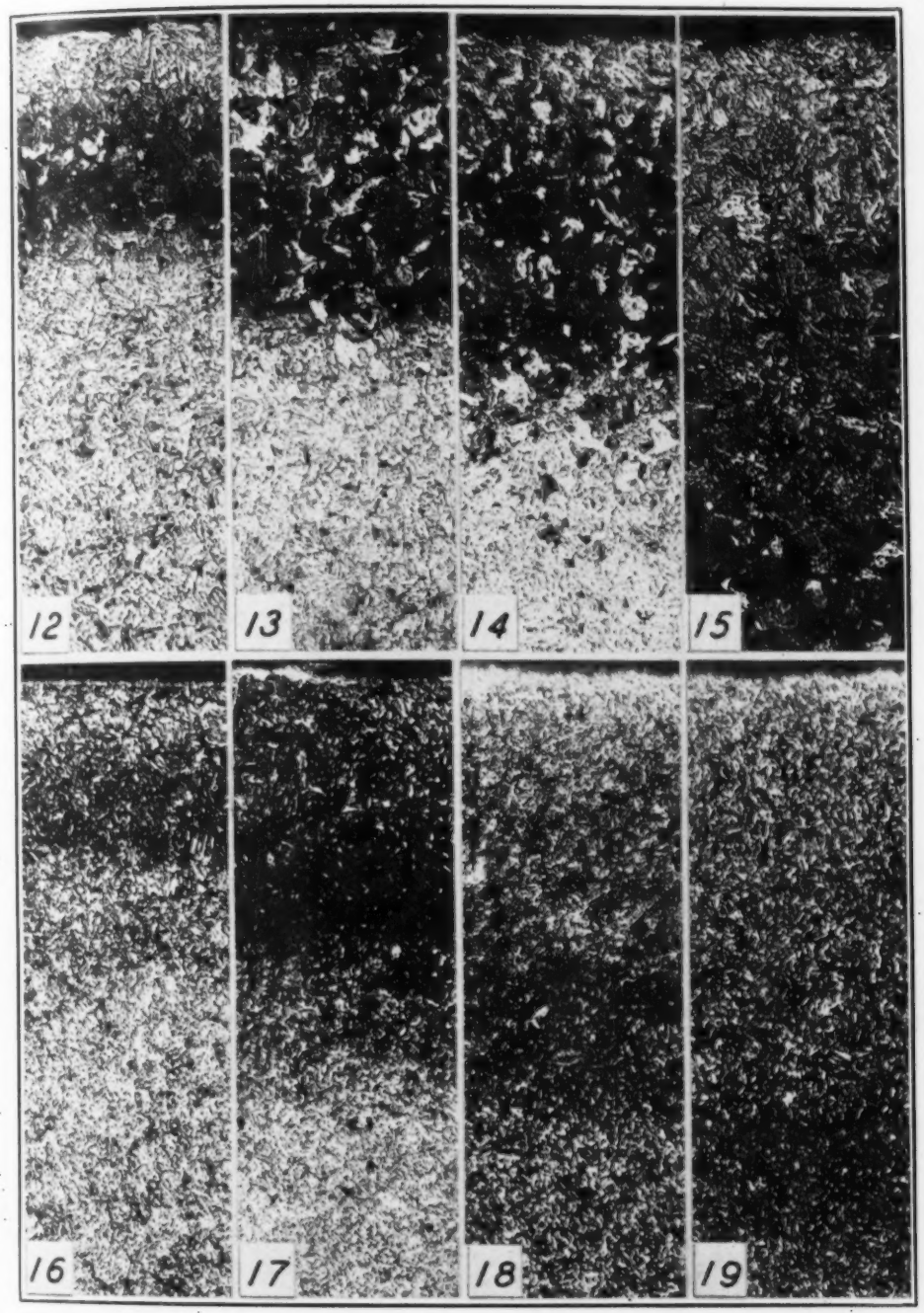
The results of these experiments tend to show that the nitriding process presents a certain amount of flexibility. Greater depth of case with less hardness is obtainable by increasing the nitriding temperature. No separation of the case into layers was detected in these experiments. Certain disadvantages in the use of a high nitriding temperature include, besides the decrease in surface hardness, the following:

1. Increased dissociation of the ammonia thereby causing the liberation of more atomic hydrogen.
2. Because of (1) and because of the higher temperature there will be a greater tendency toward decarburization due to the action of the atomic hydrogen.
3. Greater growth on nitriding.
4. Greater tendency toward distortion.

D. L. Edlund[10] has demonstrated to the authors that etching with nital does not indicate the total depth of case except where it is obtained at the higher temperatures. He has found Marbles Reagent (4 grams copper sulphate, 20 cc. hydrochloric acid, 20 cc. water) to be entirely satisfactory to show the total depth of case produced at the various temperatures.

The possibility of nitriding at a relatively high temperature to obtain a deep case and then continuing the nitriding at a lower temperature to obtain the requisite surface hardness has been stud-

[10]D. L. Edlund, metallurgist for the Ludlum Steel Co. Private Communication.



Figs. 12 to 19—Photomicrographs of Steel "G" Nitrided at 950 degrees Fahr. Specimens of Figs. 12 to 15 were Annealed and then Nitrided for 24, 48, 72 and 96 Hours Respectively. Specimens of Figs. 16 to 19 were Heat Treated and then Nitrided for 24, 48, 72 and 96 Hours. Nital Etch. × 100.

ied. Experiments have been conducted by using 1200 degrees Fahr. (650 degrees Cent.) as the higher temperature and 950 degrees Fahr. (510 degrees Cent.) as the lower one. McQuaid[11] has recently published an article in which he advocates 1200 and 975 degrees Fahr. (650 and 525 degrees Cent.) as the two advisable nitriding temperatures.

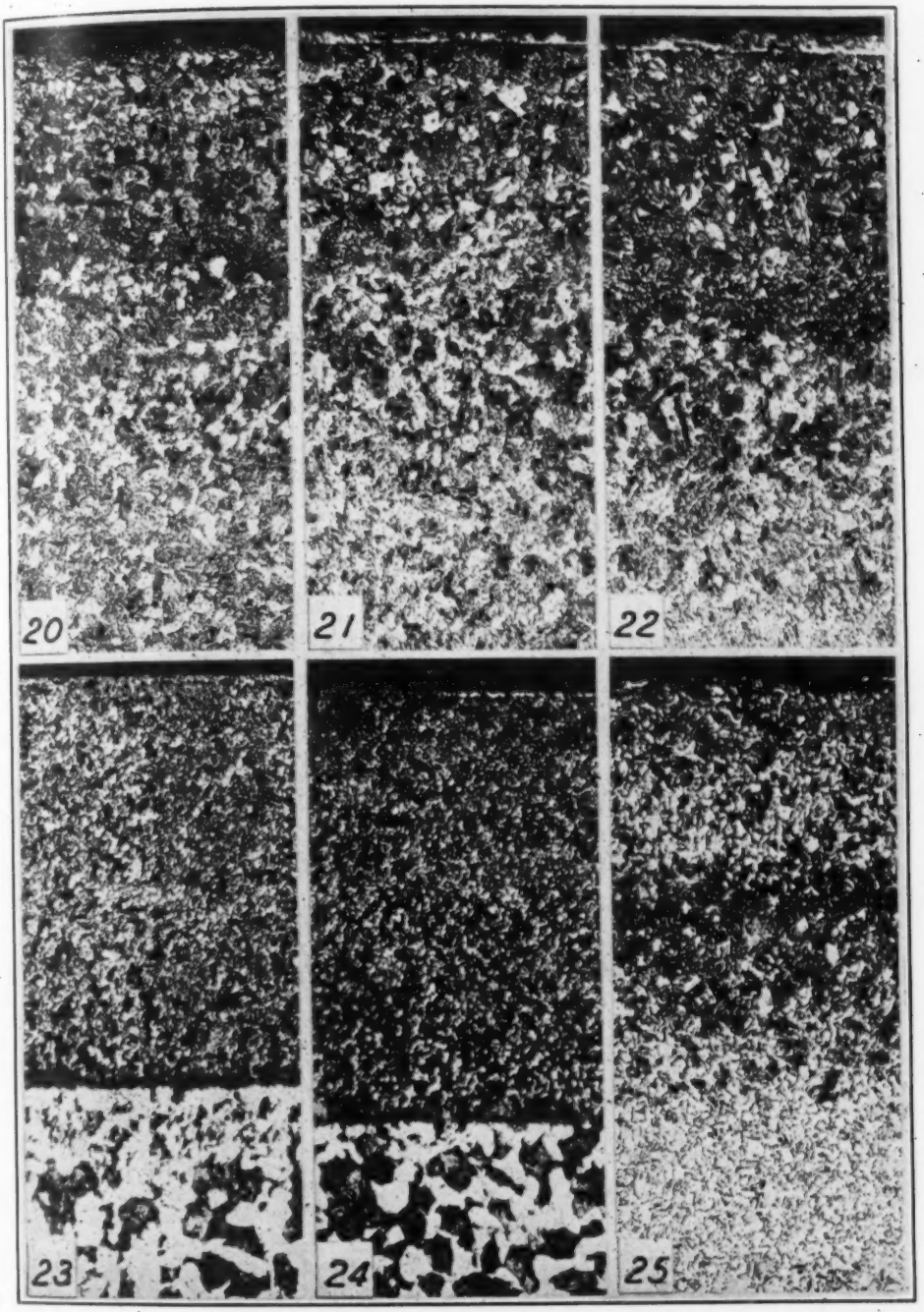
The effect of time on nitriding is shown in Figs. 12 to 19, inclusive. Figs. 12 to 15, inclusive, show the depth of case produced by nitriding annealed steel "G" for 24, 48, 72 and 96 hours respectively at 950 degrees Fahr. (510 degrees Cent.), while Figs. 16 to 19, inclusive, show the results on nitriding specimens of the same steel previously oil-quenched from 1650 degrees Fahr. (900 degrees Cent.) and tempered at 1000 degrees Fahr. (540 degrees Cent.). It is to be noted that the case etches more rapidly than the core and that the line of demarcation between the case and the core in the heat treated specimens is very difficult to determine especially in Fig. 19, in which the case occupies the greater portion of the photomicrograph.

Effect of Heat Treatment on Nitrided Steels

Three sets of specimens of steel "H", one of which was nitrided for 24 hours at 950 degrees Fahr. (510 degrees Cent.), a second set for 90 hours at 950 degrees Fahr., and the third set for 90 hours at 1200 degrees Fahr. (650 degrees Cent.) were reheated at 100-degree Fahr. intervals from 1000 to 2000 degrees Fahr. (540 to 1095 degrees Cent.), inclusive. Specimens were furnace-cooled and water-quenched from the reheating temperatures and then examined microscopically and for hardness with a Herbert pendulum. Only specimens which had been previously nitrided for 90 hours at 950 degrees Fahr. (510 degrees Cent.) will be discussed.

Fig. 20 shows the microstructure of a specimen of steel "H" which had been nitrided for 90 hours at 950 degrees Fahr., but not reheated. Fig. 21 represents the structure resulting from reheating to 1300 degrees Fahr. (705 degrees Cent.), followed by furnace cooling. The microstructure of specimens reheated to 1000, 1100, 1200 and 1300 degrees Fahr. (540, 590, 650 and 705 degrees Cent.)

[11] H. W. McQuaid, "Working Rules for Nitrogen Hardening", *Iron Age*, Vol. 123, May 9, 1929, p. 1272.



Figs. 20 to 25—Photomicrographs of Steel "H." Fig. 20 Nitrided at 950 degrees Fahr. 90 Hours. Fig. 21—Nitrided and Reheated to 1300 degrees Fahr. Furnace-cooled. Fig. 22—Reheated to 1400 degrees Fahr. Furnace-Cooled. Fig. 23—Reheated to 1800 degrees Fahr., Furnace-cooled. Fig. 24—Reheated to 2000 degrees Fahr., Furnace-cooled. Fig. 25—Reheated to 1000 degrees Fahr., Water-quenched. Nital Etch. × 100.

closely resemble that of the original material as shown in Fig. 20. Reheating to 1400 degrees Fahr. (760 degrees Cent.), followed by furnace cooling, begins to show a line of demarcation between the case and the core, as indicated in Fig. 22. This line of demarcation becomes more marked as the reheating temperature is increased. Figs. 23 and 24 show this sharp line of demarcation between the case and the core and the widening of the case as the result of furnace cooling from 1800 and 2000 degrees Fahr. (980 and 1095 degrees Cent.), respectively. Evidently considerable diffusion of the nitrogen as nitride has taken place at these elevated temperatures.

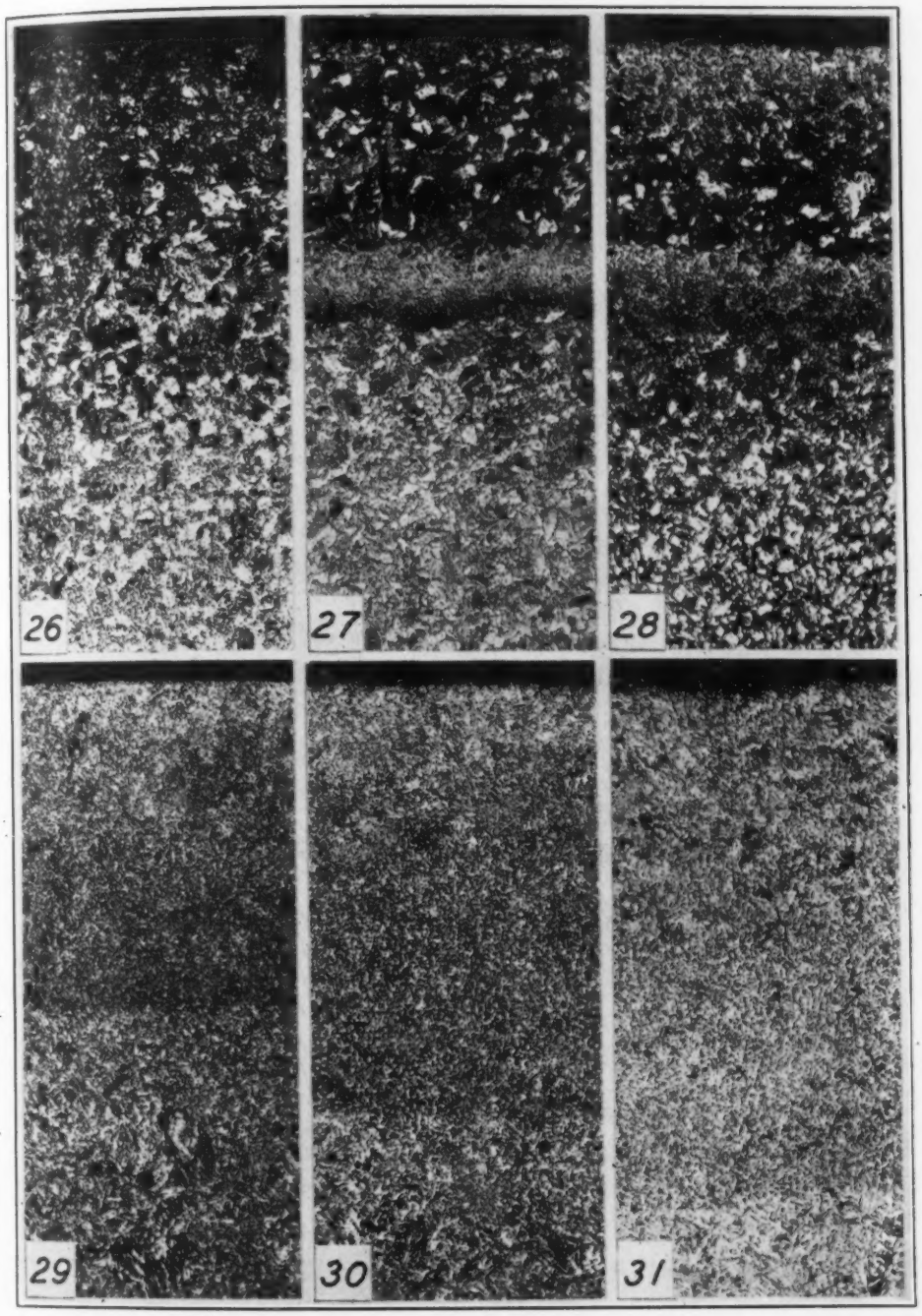
The microstructure of the specimens reheated to 1000, 1100, 1200 and 1300 degrees Fahr. (540, 590, 650 and 705 degrees Cent.), followed by water quenching, differ but slightly from the original nitrided structure. Figs. 25 and 26 represent the structures obtained by water quenching from 1000 and 1300 degrees Fahr. (540 and 705 degrees Cent.), respectively. Water quenching from 1400 degrees Fahr. (760 degrees Cent.) produces a band between the case and the core, as indicated in Fig. 27, while quenching from 1500 degrees Fahr. (815 degrees Cent.) causes a widening of this band as shown in Fig. 28. Figs. 29, 30 and 31 show the structures obtained on water quenching from 1800, 1900 and 2000 degrees Fahr. (980, 1040 and 1095 degrees Cent.), respectively. Marked grain refinement of the case has taken place and diffusion of the nitrogen at the higher temperatures is indicated.

The fact that no coarsening of the structure of the case takes place on reheating to temperatures above that at which refinement takes place may be attributed to the inhibiting action of the nitride particles to grain growth.

It is significant that the first change in microstructure for both the furnace-cooled and the water-quenched specimens is shown when the reheating temperature reaches 1400 degrees Fahr. (760 degrees Cent.). This temperature is above the Ac_1 temperature, whereas 1300 degrees Fahr. (705 degrees Cent.) is below it.

Table X indicates the hardness of the specimens as determined with a Herbert pendulum and translated into Brinell values. The letters F. C. represent furnace cooling and W. Q. signifies water quenching from the reheating temperatures.

The hardness values for the specimens furnace-cooled from 1500 degrees Fahr. (815 degrees Cent.) and above are only approximately



Figs. 26 to 31—Photomicrographs of Nitrided Steel "H." Nitrided 96 Hours at 950 degrees Fahr. Figs. 26 to 31 were Reheated to 1300, 1400, 1500, 1800, 1900 and 2000 degrees Fahr. and Water-quenched. Nital Etch. × 100.

correct because of difficulties encountered in obtaining them with the Herbert pendulum. The specimen water-quenched from 1000 de-

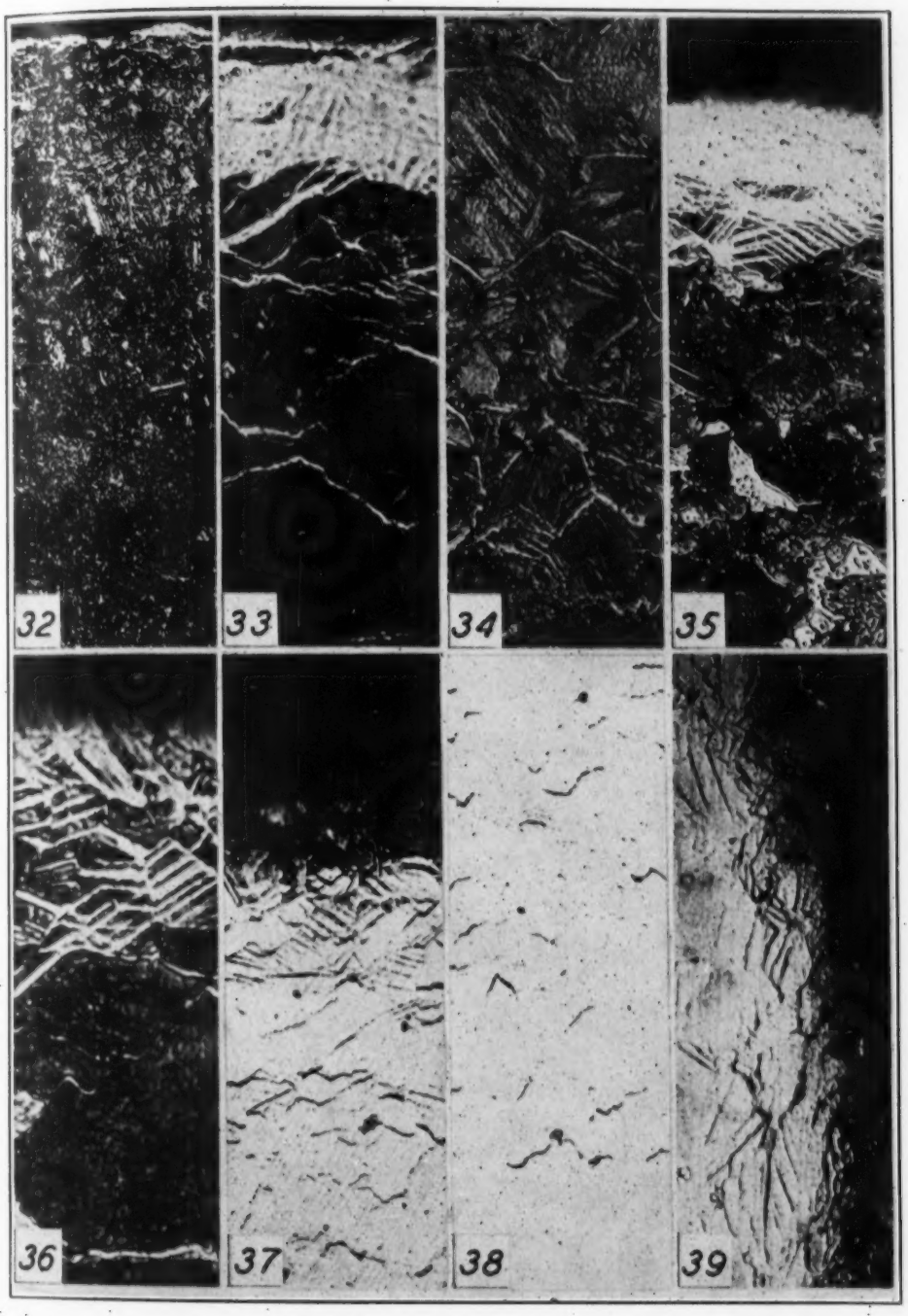
Table X
Steel "H" Nitrided for 90 Hours at 950 Degrees Fahr. (510 Degrees Cent.)

Reheating Temperatures Degrees Fahr. Degrees Cent.		Brinell Hardness
Original		965
1000 540	W. Q.	1005
1000 540	F. C.	955
1100 590	W. Q.	935
1100 590	F. C.	942
1200 650	W. Q.	920
1200 650	F. C.	920
1300 705	W. Q.	770
1300 705	F. C.	750
1400 760	W. Q.	715
1400 760	F. C.	680
1500 815	W. Q.	760
1500 815	F. C.	600
1600 870	W. Q.	750
1600 870	F. C.	600
1700 925	W. Q.	790
1700 925	F. C.	500–550
1800 980	W. Q.	765
1800 980	F. C.	500–550
1900 1040	W. Q.	790
1900 1040	F. C.	450–500
2000 1095	W. Q.	800
2000 1095	F. C.	450–500

grees Fahr. (540 degrees Cent.) shows a slight increase in hardness. The hardness reaches a minimum when water-quenched from 1400 degrees Fahr. (760 degrees Cent.), after which it increases somewhat. This temperature of 1400 degrees Fahr. is slightly above the Ac_1 point. The hardness of the furnace-cooled specimens gradually decreases with the reheating temperature.

A Study of the Nitride Constituent

A white layer at the periphery of the case is quite often observed when ammonia case hardened specimens are examined mi-



Figs. 32 to 39—Photomicrographs of Steel "G." Figs. 32 to 34—Heat Treated then Nitrided at 1100 degrees Fahr. for 48 Hours. Fig. 32 × 100. Fig. 33—Same as Fig. 32. × 500. Fig. 33—Same as Fig. 32 Near Edge, × 500. Figs. 35 to 39—Annealed Steel Nitrided at 950 degrees Fahr. for 48 Hours. Fig. 35, Nital Etch. × 500. Fig. 36, Nital Etch. × 1000. Fig. 37, Sodium Picrate Etch. × 500. Fig. 38, Same as Fig. 37, Short Distance from Edge. × 500. Fig. 39, Heat Tinted. × 500.

croscopically. This layer is often accompanied by a white network and narrow white bands.

Fig. 32 shows the white layer and the ribbon-like structure at the edge of a specimen which had been heat treated and then nitrided at 1100 degrees Fahr. for 48 hours. Figs. 33 and 34 show this type of structure at a magnification of 500 diameters. This white band and network represent a very brittle structure.

Figs. 35 and 36 show this white constituent at 500 and 1000 diameters respectively. This specimen was annealed steel "H" nitrided at 950 degrees Fahr. for 48 hours. In order to determine whether or not this white constituent is a nitride, this specimen was etched with alkaline sodium picrate. It was then repolished and heat tinted. Figs. 37 and 38 show the effect of the sodium picrate etch. The white layer, the narrow banded structure and the broken network were all etched dark. Fig. 39 shows the effect of heat tinting. The iron nitride needles in Armco iron, which was nitrided under the same conditions, responded to the etch and to heat tinting in the same manner as the white constituent in steel "H". As the result of these observations, it is concluded that this white structure is a nitride, either iron nitride or a complex one involving iron and one or more of the alloying elements.

It has been noted on many occasions that the network structure is more likely to form in the annealed than in the heat treated material on nitriding. This is to be expected since in the annealed material the grain boundaries are generally well defined. Figs. 40 and 41 show the structures of the core and the case respectively of annealed steel "H" after nitriding. Well defined grain boundaries are evident in the core and the presence of the nitride network is clearly indicated in the case.

Since the presence of the nitride constituent represents brittleness and is especially harmful when present as a network in articles which are subject to any shock, it is evident that every precaution should be taken to avoid this structure as much as possible.

Figs. 42 and 43 show the microstructures of steel "G" which was heat treated and then nitrided at 950 degrees Fahr. for 48 hours. Fig. 43 shows the fine sorbitic structure of the core, while Fig. 42 indicates the complete absence of the nitride network in the case. An additional reason for heat treating the steel so as to obtain a sorbitic structure before nitriding is to eliminate as far as possible the tendency towards the formation of the nitride network.

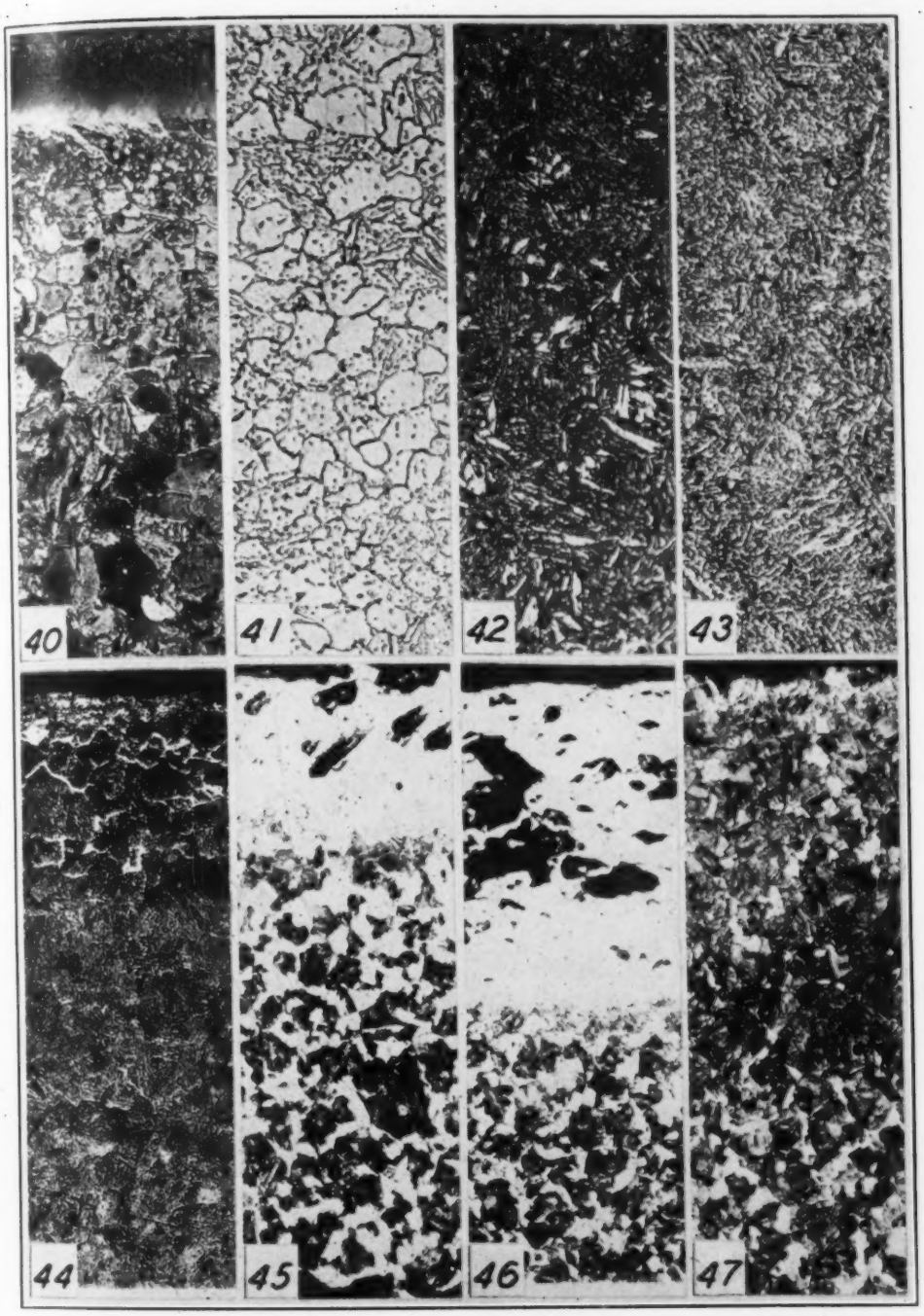


Fig. 40—Annealed Steel "H" Nitrided 96 Hours at 950 degrees Fahr. Nital Etch. × 500.

Fig. 41—Core of Fig. 40. × 500.

Fig. 42—Case Obtained by Nitriding Heat Treated Steel "G" at 950 degrees Fahr. for 48 Hours. Nital Etch. × 500.

Fig. 46—Decarburized 0.010 Inch and treated as Fig. 45. × 100.

Fig. 44—Steel "G" Nitrided at 1000 degrees Fahr. for 48 Hours with 90 per cent Ammonia Dissociation. × 100.

Fig. 45—Decarburized and then Nitrided for 90 Hours at 950 degrees Fahr. × 100.

Fig. 43—Core of Fig. 42. × 500.

Fig. 47—Decarburized, the Decarburized Layer Removed and Steel Nitrided 90 Hours at 950 degrees Fahr. Nital Etch. × 100.

The factors which are of importance in the study of this phase of the nitriding problem include:

1. The condition of the steel before nitriding
2. The nitriding temperature
3. The extent of the ammonia dissociation
4. The analysis of the steel
5. The use of catalysts.

The effect of the condition of the steel before nitriding has been mentioned.

No conclusive proof as to the effect of the nitriding temperature and the extent of the ammonia dissociation has been determined. However, a specimen of steel "G" nitrided at 1000 degrees Fahr. (540 degrees Cent.) for 48 hours with an average ammonia dissociation of 90 per cent showed a large amount of the nitride network, as indicated in Fig. 44.

No results can be given at this time with regard to the analysis of the steel, since only those steels, the analyses of which are given in Table I, have been investigated.

The use of catalysts should be studied carefully. Some investigators report very deep cases by their use.

The relation of the diffusion of the nitrogen to its absorption must receive careful consideration in a study of this phase of the problem. The authors have used certain nitrogenous compounds together with the ammonia gas and have obtained a marked network structure in a number of instances.

A thorough microscopic study of the nitrided specimens should be followed in an investigation of this problem, as a deep case is not the only desired result. The character of the case is of the utmost importance in order that brittleness may be eliminated as far as possible and greater toughness obtained.

Effect of Decarburization on Nitriding

Great emphasis should be given to the necessity for the complete removal of any decarburized layer before nitriding. Flaking and chipping of the case will result if this precaution is not observed. In order to illustrate this fact, samples of steel "G" were decarburized by heating in an oxidizing atmosphere at a temperature of 1650 degrees Fahr. (900 degrees Cent.) for 6 hours. After the removal of the scale, the specimens were machined so that each

succeeding sample was made smaller than the preceding one by 0.010 inch. The specimens were then nitrided at 975 degrees Fahr. (525 degrees Cent.) for 90 hours. The results of this experiment are indicated by the photomicrographs in Figs. 45, 46 and 47. Fig. 45 shows only part of the brittle case in the decarburized layer as a great deal of it had flaked off in the furnace. Fig. 46 shows the appearance of the case after the removal of 0.010 inch before nitriding, while Fig. 47 shows the structure of the case after the complete removal of the decarburized zone before nitriding. The black areas in the first two photomicrographs represent voids.

Sufficient material must be left for final machining or grinding before nitriding to insure the complete removal of all traces of decarburization resulting from the forging and the heat treating operations.

A typical procedure to follow in the case of an article machined from an annealed bar is to rough machine, heat treat, finish machine and then nitride. The rough machining should remove all of the decarburization. Special precautions to remove the decarburized layer should be taken whenever the rough machining is applied to forgings.

The heat treatment involves quenching in oil from the hardening temperature, followed by a temper at least as high as the nitriding temperature to obtain proper physical properties for the core and to relieve machining and hardening strains. The tempering temperature generally varies from 1000 to 1250 degrees Fahr. (540 to 670 degrees Cent.). Sufficient time should be allowed for this operation to insure the complete removal of strains in order to prevent warping or distortion of the articles on nitriding. The final machining or grinding should remove all traces of decarburization before nitriding.

Protection Against Nitriding

It frequently happens that threaded portions or other parts of articles must be protected against nitriding. Nickel plating to a depth of at least 0.0005 has proved to be satisfactory. A coating of tin or tin solder is also an effective protective agent. Although tin melts at a temperature considerably lower than the nitriding temperature, a sufficient amount will adhere by surface tension to provide ample protection.

Parts to be protected against nitriding should be cleaned, then

dipped into the molten tin or solder and kept there for a time sufficient to heat the parts somewhat so that the tin will not solidify immediately on the removal of the parts from the bath. The excess tin or solder can be shaken off or removed with a wire brush. If this precaution is not observed, particles of molten tin will drop onto articles at a lower level in the nitriding box and produce soft spots. The parts should be cleaned and a flux applied before dipping into the molten tin or solder. The flux used has the following composition:

Hydrochloric acid	500 cc.
Water	250 cc.
Ammonium Chloride	15 grams

Add zinc until no further action takes place. The articles to be tinned must be free from rust or scale.

It is obvious that a protective agent, which might be applied as a paint, is highly desirable. The authors have experimented with a great many materials, including oxides, cements, etc. Positive results have been obtained in the use of stannous and stannic oxides (tin oxides). These compounds decompose in the nitriding furnace to form tin. The spraying of a suspension of the oxide in a suitable vehicle makes it possible to obtain a very thin coating. Care must be exercised that the vehicle does not react with the tin oxide or in any manner to prevent its decomposition. Also, too much of it must not be applied as some may then drop off onto articles at a lower level in the box and produce soft spots where protection is not desired.

Resistance to Corrosion

A valuable property which accompanies the extreme surface hardness of nitrided steels is its resistance to atmospheric, water and salt water corrosion. Experiments were performed in which specimens were nitrided at 900 degrees Fahr. (480 degrees Cent.) for varying lengths of time and then subjected to the action of water and salt water sprays. The concentration of the salt solution was 20 per cent. The first indication of a corroded area was noted in each case.

The general appearance of the samples indicates that 48 hours nitriding at 900 degrees Fahr. (480 degrees Cent.) prevents corrosion in salt spray and that nitriding for 24 hours will give very good resistance to water spray corrosion. Specimens nitrided for 90 hours withstood the action of the salt spray for over 100 hours. Additional

experiments may show that shorter periods of nitriding at higher temperatures can be used to give satisfactory results.

The maximum resistance to corrosion is exhibited by the unpolished surface. In view of this fact, it is preferable to place nitrided articles directly into service without polishing whenever the question of corrosion is involved.

Although excellent resistance to atmospheric, water and salt water corrosion has been reported from a number of sources, somewhat erratic results are sometimes obtained. Localized pitting has been observed in some instances. The authors' first thought to account for this pitting was to associate the pits with the possible presence of inclusions at the surface whereby a break in the case might be expected. Close observation failed to substantiate this explanation. It must not be inferred, however, that the presence of inclusions may not be responsible for poor corrosion resistance. The nitriding of dirty steel will certainly give inferior results. Another possible cause for localized corrosion might be the embedding of particles of a plain carbon steel as the result of the preparation of the specimens on a grinding wheel and on emery belts which had been used previously in preparing other steels. Improper nitriding would take place at such points.

Another possible explanation of the cause of local pitting is the formation of gas bubbles which may be held on the surface of the metal in a manner analogous to the formation of bubbles on a piece of hot metal when it is immersed in water. These bubbles may cause faulty nitriding with consequent lowering of the resistance to corrosion at these places. Active circulation of the ammonia gas, a principle incorporated in one of the industrial nitriding furnaces now on the market, may prevent the formation of such areas. This entire problem is being thoroughly investigated at the present time. Although erratic results have been reported at times, steels properly nitrided possess marked resistance to atmospheric, water and salt water corrosion.

Growth on Nitriding

A slight growth takes place during nitriding. Table XI shows the increase in length and in diameter of cylinders of steel "G," previously oil-quenched from 1650 degrees Fahr. and tempered at 1000 degrees Fahr. for 6 hours followed by nitriding at the indicated temperature for 48 hours. Prior to nitriding, these cylinders were

Table XI
Growth of Steel "G" on Nitriding

Samples Heated to 1650 Degrees Fahr. for One Hour. Oil-quenched. Tempered at 1000 Degrees Fahr. for 6 Hours. Accurately Ground, Then Nitrided for 48 Hours at Indicated Temperature.

Nitriding Temperature Degrees Fahr. Degrees Cent.	Increase in Length in Inches	Increase in Diameter 1st End	Middle	2nd End
900 480	0.001	0.00038	0.00028	0.00029
950 510	0.002	0.00100	0.00092	0.00117
1000 540	0.003	0.00202	0.00111	0.00183
1100 590	0.007	0.00197	0.00178	0.00321
1200 650	0.020	0.00470	0.00181	0.00403
1300 705	0.020	0.00535	0.00174	0.00464

accurately ground after which they measured approximately 5.80 inches in length and 0.70 inches in diameter. The exact length and diameter were accurately measured in each instance.

On measuring each cylinder after nitriding it was found that the diameter at the ends had increased a great deal more than at any other point. This is due to the "corner effect" which also prevented the accurate determination of the increase in length. The growth of the cylindrical surface together with the growth of the circular section had combined to push the edge outward. The total effect was too small to be seen but measurement showed this to be true. The obvious correction for this increased growth is to provide well-rounded corners wherever possible.

The general growth can be allowed for in the final machining or grinding before nitriding, or it can be removed afterwards by lapping or by some other suitable means.

Summary and Conclusions

The results of the tests to determine the physical properties of the chromium-aluminum steels show that they compare favorably with such structural alloy steels as are used in automotive construction. High physical values are also shown by these steels after nitriding followed by testing both at room temperature and at elevated temperatures.

Nitriding at 950 degrees Fahr. (510 degrees Cent.) has little or no influence on the hardness and impact properties of the core of the steels provided that these steels have been hardened and then

tempered at 1000 degrees Fahr. (540 degrees Cent.) or above.

The chromium-aluminum steels are not susceptible to temper brittleness. The presence of molybdenum tends to toughen both the case and the core.

All parts should be heat treated so as to obtain a sorbitic structure before nitriding. This treatment is recommended in order to obtain desirable physical properties of the core and to insure proper grain refinement since the original grain size of the material is not reduced during the nitriding operation. A sorbitic structure is recommended also in order to eliminate as far as possible the formation of a nitride network which is quite likely to form in nitriding the annealed material in which the grain boundaries are well defined. It is obvious that the nitriding of an article exhibiting a coarse grain structure will produce a very brittle case.

Nitriding at temperatures ranging from 800 to 1400 degrees Fahr., inclusive, shows that the depth of case increases with the nitriding temperature from 800 to 1300 degrees Fahr. (425 to 705 degrees Cent.), inclusive, but drops off slightly at 1400 degrees Fahr. (760 degrees Cent.). The hardness decreases as the nitriding temperature increases. It is possible to nitride at a relatively high temperature, 1200 degrees Fahr. (650 degrees Cent.) for example, to obtain considerable depth of case and then to nitride at a lower temperature, such as 950 degrees Fahr. (510 degrees Cent.) to obtain the desired surface hardness.

The white layer frequently seen at the periphery of nitrided specimens when examined microscopically is a nitride of iron or a complex nitride of iron and one or more of the alloying elements. The narrow white bands and the white network, both of which often accompany the white nitride layer, represent the same constituent, the presence of which produces brittleness. This structure, especially the network, should be avoided as much as possible. As previously stated, it is more likely to form in the annealed steels than in those having a sorbitic structure. The degree of dissociation of the ammonia and the nitriding temperature are also important factors.

Nitrided specimens reheated at 100 degrees Fahr. intervals from 1000 to 2000 degrees Fahr. (540 to 1095 degrees Cent.), inclusive, followed by furnace cooling and water quenching, show changes in microstructure after passing the Ac_1 point of the steel. Furnace-cooled specimens show an increasing tendency toward a sharp line of demarcation between the case and the core with increase in tempera-

ture above 1400 degrees Fahr. (760 degrees Cent.). The water-quenched specimens first show a banded structure and then a widening of the case zone together with refinement of grain structure with increase in temperature on reheating above the Ac_1 point.

The hardness of the specimens which were reheated, then slowly cooled, gradually decreases as the reheating temperature is increased. The quenched specimens show maximum hardness after quenching from 1000 degrees Fahr. (540 degrees Cent.) and a minimum at 1400 degrees Fahr. (760 degrees Cent.).

The presence of decarburization before nitriding produces a brittle case which is likely to spall or chip. This decarburized layer must be removed before the subjection of the parts to the action of the ammonia gas.

Strains created by machining and heat treating of parts must be eliminated if warping or distortion in the finished articles is to be prevented.

Nickel plating and a coating of tin or solder will protect parts against nitriding. A coating of stannous or stannic oxide will also serve as a protective agent.

A slight growth takes place during nitriding. Allowance can be made for this growth in the final machining or grinding operation before nitriding or by lapping or by other suitable means after nitriding.

Nitrided articles offer marked resistance to atmospheric, water and salt water corrosion.

The evolution of this new series of alloy steels together with the method of case hardening these steels with ammonia gas to obtain extraordinary surface hardness without warping or distortion of the treated articles, the retention of this hardness at elevated temperatures and the marked resistance of nitrided articles to atmospheric, water and salt water corrosion, represents one of the most important metallurgical developments in recent years.

The future development of the nitriding process and a full realization of all its advantages over the older case hardening methods can be brought about by the application of the basic sciences to the study of the problem. The scientific study must be accompanied by practical tests in order to put the process on a sound economic basis.

Acknowledgment

The authors are indebted to the Ludlum Steel Company for the

materials used in this investigation. The complete co-operation of the various members of the metallurgical staff of this company, especially that of D. L. Edlund, is greatly appreciated. The authors also wish to express their appreciation to I. N. Zavarine of the Massachusetts Institute of Technology for his aid in conducting the physical tests.

DISCUSSION

Written Discussion: By V. T. Malcolm and J. W. Juppenlatz, Chapman Valve Co., Indian Orchard, Mass.

Under the heading of resistance to corrosion, page 99 of Messrs. Homerberg and Walsted's contribution, they report that localized pitting has been observed in some cases, and their first thought was to associate these pits with the presence of inclusions at the surface whereby a break in the case might be expected. They claim that close observation failed to substantiate this explanation, and give as a possible cause the imbedding of carbon steel particles as the result of preparation of the specimens. However, on page 96 they consider as an important factor the condition of the steel before nitriding, and yet on page 99 they state that, although erratic results have been reported at times, steels properly nitrided possess marked resistance to atmospheric, water and salt water corrosion.

The writers are at loss to understand these statements without any evidence being produced, and as the writers believe they originally discovered and reported the pitting of nitrided steel and in their study of this condition, they feel sure that it is caused by dirty steel. They are still of the same opinion particularly after the evidence has been checked by a number of well known metallurgists.

(1) Messrs. Homerberg and Walsted state that those carbon steel particles are imbedded before nitriding, and if so, we can consider these particles as inclusions, analogous to impurities in the steel.

(2) When specimens were polished either before or after nitriding, belts and cloths used were new.

(3) If their statement is correct, would not particles from grinding wheels or belts imbed themselves rather than the softer steel from a loaded wheel?

(4) Again if their statement is correct we would have to have a special operation in the shop peculiar to steel for nitriding and on which no other type of work could be done; which of course is out of the question.

(5) Because the facts brought out by our investigations show their statement is not correct, and that inclusions at the surface of the steel do produce a discontinuity that is not possible to nitride. Dr. Homerberg substantiates this fact when he states carbon steel imbedded causes pitting, whereas our claim is that inclusions in the original steel caused pitting.

(6) Evidence obtained by deep etching of good and bad samples, nitriding and subjecting these samples to a corrosion test, plainly shows the erratic behavior of steel containing inclusions.

Procedure and Results

It was found that certain soft spots and selective corrosion ("pitting") in nitrided steel was caused by the quality of the steel.

We noticed in connection with our work that "pitting" occurred only in bars of steel obtained from certain melts, which in our opinion may be termed "off quality" steel.

Of course, the expression quality as used in steel manufacture is an indefinite term, but a glance at recent specifications undoubtedly shows that it is being given serious attention. The term "quality" is only of value if used in comparison of certain steels made by the same process and is usually compared by means of certain laboratory tests, and from the results of these tests an index as to its quality may be determined. This so-called quality depends largely on the amount and nature of the inclusions and the form in which they are present. The effect of inclusions also depends to a great extent on whether they occur alone or in the presence of others.

The deleterious character of these inclusions is coming more and more to be recognized, even if their presence to a limited extent must be accepted as more or less unavoidable in commercial steels. However, we do not expect a high grade alloy steel for nitriding to have inclusions amounting to an extent similar to the common or cheaper steels.

The influence of inclusions on the properties of nitrided steel is a problem still requiring much investigation and depends to a great extent on the accurate estimation of the amount present, as to what constitutes a dirty steel and is still a matter of opinion, but the fact remains that while inclusions cannot be eliminated they may be prevented. Once dirty steel has solidified nothing can be done to remedy it.

We are convinced that steel containing inclusions of this peculiar type cannot in our ordinary routine work be properly nitrided, without certain discontinuities in the nitrided case. We believe these inclusions to be oxides either in solution or colloidal particles. We of course expect considerable controversy over the subject as to the nature of these inclusions, but there is no doubt in our minds that the cause of pitting is due to aluminum as oxide or as a compound of iron and aluminum oxides, and while it seems to be the fashion of late to say that troubles encountered with steels are due to oxides, and sometimes the importance of inclusions has been over-emphasized, but there is a vast amount of truth in the statement that considerable of the troubles encountered are due to dirty steel, and there is no doubt that when clean, sound steel is produced we will go a long way toward safety and economy.

It is usually assumed that chemical specifications are sufficient for a steel to be used for nitriding, and if the steel is within the ordinary limits specified, no difficulty traceable to the steel should be encountered in obtaining satisfactory and duplicate results in nitriding. This, Dr. Homerberg leads us to believe when on page 99 he states that steels properly nitrided possess marked resistance to atmospheric, water and salt water corrosion.

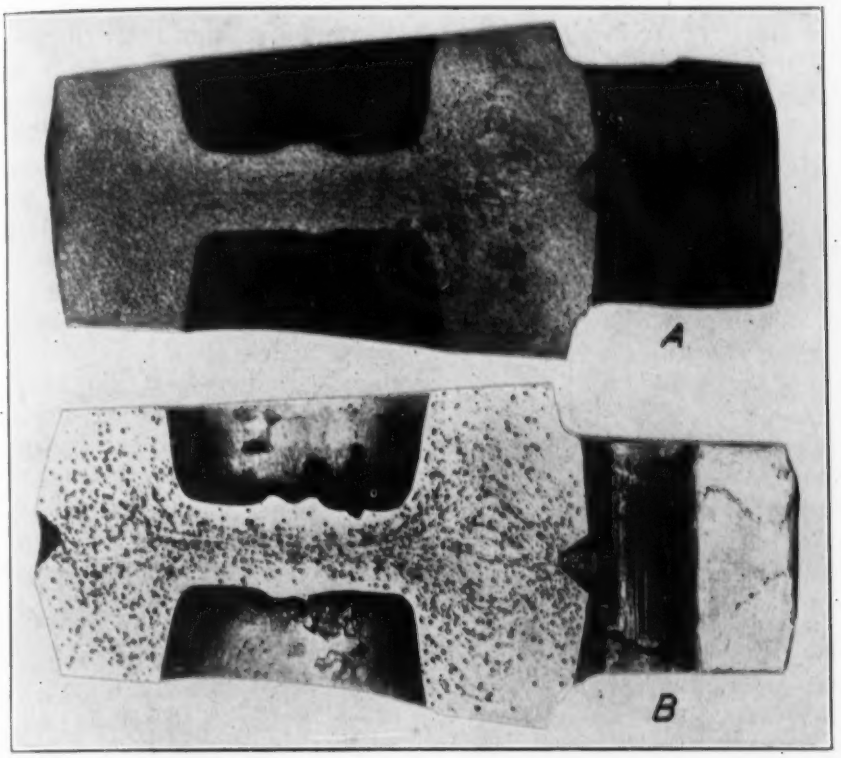


Fig. 1—Plugs Made of Aluminum-Chromium Steel. A—Etched with 20 Per Cent Sulphuric Acid. B—Etched with 2 Per Cent Nitric Acid Plus 10 Per Cent Hydrochloric Acid.

However, during the past it was apparent from our chemical analysis that we did not even obtain chemical composition within ordinary standard practice, and we know that a steel for nitriding containing 0.60 per cent aluminum will certainly not nitride along with a steel containing 1.40 per cent aluminum and obtain the same results in both heats after nitriding, and we note with interest that Dr. Homerberg's results as published have been based on steels having aluminum above 1 per cent except in the case of "I" grade of steel.

There is no doubt that in the manufacture of this type of steel that unless great care is exercised some of the aluminum remains in the steel as an oxide or as a complex iron-aluminum compound, and appear in the polished specimen as hard, brittle particles, and from our investigation it is evident that the nitriding treatment has no effect on these particles, and, therefore, we believe that the nitriding of steel is greatly affected by the actual condition of the steel as cast, and that for reliable results in the nitriding operation the steel should be of the best possible quality as regards to freedom from inclusions. We speak in this connection not only from a laboratory point of view, but as among the original users of this treatment and in all probability the largest individual users of nitrided steel at present in the country and this after a period of more

than two years' work with hundreds of tons of this steel, so we believe we are more able to dwell on actual conditions than on a few experimental results.

Macroscopic and microscopic examination of many specimens of this type of steel before and after nitriding developed a striking difference between steels which would show soft spots and those that would be satisfactory. By careful comparison of steel that produced poor results with steels that gave satisfactory results it became possible to determine whether or not, after nitriding, the steel would have these soft areas subject to water corrosion with the pitted effect, and in this connection it might be well to state that results obtained varied with different heats that were either quality or off quality heats.

This comparison method seemed to offer a means of checking and eliminating off quality steel; as it only became necessary to place upon the purchase of this steel specifications as to quality and which specifications the steel makers agreed, was not too rigid for them to meet without difficulty, although some objections were raised in one instance.

The purpose of the investigation was then to determine a proper etch test that if interpreted correctly would be of great value in separating satisfactory from defective steels because it reveals:

(1) Physical discontinuities existing in the metal
(2) Chemical discontinuity
(3) Conditions of strain.

Naturally the action of the hot acid etch accentuates these defects.

The various physical discontinuities we are able to discover by etching are cracks, seams, blowholes and pipe. All such defects are obviously objectionable and are not present in satisfactory metal.

Chemical discontinuities include chiefly segregation of metallic material as well as nonmetallic impurities.

Usually, both kinds of segregation occur together and are revealed by etching as large pits or are discolored differently from the main part by etching.

Strain areas are accentuated to a point of rupture by the action of the acid and material strained before etching, but not cracked, will appear cracked after etching.

There is no test, shearing or otherwise, that will show up defects as the acid etch.

Discussion of the acid etch usually consists largely in criticism of improper use, the technique of application and the interpretation of results. We do not know of any definite criticism of this test when properly applied and when the interpretation is made with a moderate amount of common sense.

The writers have used the hot acid etch in the inspection of special steels for the past eight years, and while in the beginning there was some reluctance on the part of the steel maker, we found they were willing to co-operate in the manufacture of steel purchased under the acid etch

specifications, so that now the steel purchasers not only make steel to meet the acid etch specifications, but quite a few of them have adopted it as regular routine inspection in their own mills on important work (and in fact we note with interest one concern advertising in the TRANSACTIONS of September, 1929, states that all special steels are acid-etched and

Fig. 2—Plugs Made of Aluminum-Chromium Steel. A—Etched with 20 Per Cent Sulphuric Acid. B—Etched with 2 Per Cent Nitric Acid Plus 10 Per Cent Hydrochloric Acid.

labeled to the effect that the disk passed inspection) because its value as an inspection standard has now been recognized and it certainly forestalls rejections.

This fact alone is conclusive proof as to its value and establishes a test for consumers, by which the quality of metal is shown.

MACROSCOPIC ETCH AS USED FOR STEELS FOR NITRIDING

As steel for nitriding differs to a considerable extent from other steels it was necessary to determine a proper etching reagent. Combinations of hydrochloric and sulphuric acids in various quantities were

tried but apparently did not have the desired effect. Combinations of other acids were used till finally a solution of 2 per cent nitric acid and 10 per cent hydrochloric acid was tried at 180 degrees Fahr. for one hour. This combination of acids worked very satisfactorily on steels used for nitriding attacking aluminum inclusions and leaving pits, but not attacking the steel to any great extent.

In carrying out this investigation all specimens were from the same bar and tested under the same exacting conditions.

This acid etch was finally adopted and with this reagent it has been possible to correlate the macroscopic with microscopic examinations.

In the macro-etch a certain black deposit taken from pits showed on chemical analysis as much as 46 per cent Al_2O_3.

Microscopic Investigation

The method used in preparing the specimens for microscopic investigation was as follows:

Light grinding on fine emery wheel.

Flattening of surface by hand grinding on oil-stone.

Grinding by hand or French emery paper beginning with No. 1 and ending with No. 0000 and the pressure exerted was very light to practically nothing on the fine papers.

Polishing on a disk covered with canvas and charged with jeweler's rouge against a revolving wheel. Very little pressure was exerted on the specimen at any time during polishing.

Specimens were carefully washed in benzine and alcohol and finally polished on wheel covered with kitten's ear broadcloth charged with a paste of the finest magnesium oxide.

By careful manipulation, inclusions were found to be in good condition for examination. On examination under the microscope it was found that certain inclusions appeared and in order to test as to whether they were inclusions or pits the following procedure was adopted:

The lens was focused on the bottom and if an inclusion it will remain dark, simply fading in clearness, if it is a pit bright areas will appear when the lens is focused on bottom in the form of interference rings which are the result of light reflection from the walls of the cavity, and no material inclusion is capable of producing this result.

Considerable of the inclusions found have all the mark of aluminum compounds, and which we believe they are, for the following reasons:

(1) Inclusions of a hard substance were seen in bright relief on the polished surface.

(2) Inclusions were extremely difficult to polish without pitting.

(3) The inclusions were always small particles and were never coalesced into larger bodies regardless of how closely grouped.

(4) The hardness and brittleness account for the pitting in polishing unless carefully polished.

(5) The infusibility of aluminum compounds would account for small size of particles and tendency not to coalesce.

(6) The particles were attacked by sodium hydroxide and nitric acid.

(7) Silicate inclusions when found were not difficult to polish and were elongated in direction of rolling or forging. Silicate inclusions were found to be quite large as well as small and were of a distinctly dark green, with a greasy appearance.

(8) Iron oxide inclusions are medium gray in color and appear as small round particles.

(9) Stannous chloride dissolved iron oxide inclusions.

(10) Dilute hydrofluoric acid dissolves the silicate inclusions.

In closing this discussion it must be remembered that this investigation is a research assignment still incomplete, and that most of the steel offered meets satisfactory tests.

Thanks are due to F. B. Lounsberry of the Atlas works of the Ludlum Steel Company and Messrs. Morris and Sergeson of the Central Alloy Steel Company for their experimental work and co-operation in the manufacture of quality steel for nitriding.

Authors' Closure

It is possible that the paragraph referred to by Messrs. Malcolm and Juppenlatz contains an ambiguous statement with regard to the effect of inclusions on the tendency to produce localized pitting when nitrided specimens are subjected to corrosion tests. A statement has been added to the original paper in order to clarify our viewpoint. It is perfectly obvious that anything which causes a break in the nitrided case will tend to make the nitrided material subject to localized pitting. The thought which the authors wished to emphasize is that localized pitting may occur at points free from inclusions. It is evident that this was our thought since the possibility of the presence of protective gas pockets at these points is given consideration. An authority on the subject of the behavior of gases agrees with us that such a cause for the production of improperly nitrided areas is entirely possible. This theory receives further support by the fact that the use of circulating ammonia in nitriding has materially aided in eliminating the production of localized pitting on subjection of the nitrided specimens to corrosion tests.

We agree entirely with Messrs. Malcolm and Juppenlatz that steel for nitriding must be of very good quality in order to obtain satisfactory results, especially when resistance to corrosion is an important factor.

Messrs. Malcolm and Juppenlatz call attention to the fact that the steels which we investigated, with one exception, contain over one per cent aluminum. Again, we agree with them that a steel containing 0.6 per cent aluminum will not give the same results as one containing over one per cent. The presence of nitride needles has been observed after nitriding specimens containing approximately 0.5 per cent aluminum.

Over a considerable period, the steel used by Mr. Malcolm was made by the company for which one of the authors is a consultant. Only electric fur-

nace steel is made at this plant. To our knowledge, no complaints were ever made as to the quality of the steel during this period.

At the present time, this steel is made both by the basic electric and by the basic open-hearth processes. It is entirely possible to make this steel of just as good quality as any other high grade alloy steel. This is being done at the present time.

THE NITRIDING PROCESS

By Dr. Adolph Fry

Abstract

This paper deals with a discussion of results and with the possibilities of the development of the nitriding process. It discusses the practical results which have been obtained. Then it considers the influence of high pressure nitriding and especially the influence of nitriding at high temperatures. The author deals briefly with the theory of nitriding and suggests some proposed theoretical work still to be done, and gives some results of research concerning the theory of nitriding hardness. The paper gives a theoretical discussion of the mechanism of nitriding hardness. Problems which need still further study are pointed out.

Introduction

IN 1926 the writer had the pleasure of receiving in Essen your president, Dr. Zay Jeffries, and of discussing with him certain metallurgical questions. When we came to the discussion of nitriding, Dr. Jeffries stated his belief that America offered the field for the most rapid development of this process. At that time the United States had not yet entered into practical industrial application of the process. Nevertheless, Dr. Jeffries' prediction, which was based on the possibilities of your immense country, has been borne out in fact.

Since 1926 many scientific and practical investigations have been made on this process, and the great desire on the part of American steel manufacturers and scientists to probe the process and find its most interesting applications has brought satisfying results. This is particularly due to the collaboration of metallurgists of America, France, and Germany.

May I not refer also to the presence here of my friend, Pierre Aubert? Since the first appearance of the nitriding process, seven years ago, he has constantly kept up his enthusiasm for researches as well as for the practical applications, and I thank him cordially

The author, Dr. Adolph Fry, is connected with the Krupp Laboratories, Essen, Germany, and is the originator of the nitriding process. Manuscript received September 13, 1929.

for having furnished unceasingly all the technical and practical aid of his firm in Paris. In 1926, at your Chicago convention, he came as first missionary to tell you of the practical results already obtained in Europe in a great number of industries, namely, automobile, aviation, railroad, textile, machine tools, etc.

I have listened with much pleasure to the presentation of the papers this morning, and anticipate hearing those to be given this afternoon. I am glad to say that all of the results—with few exceptions which I will mention later—are in complete agreement with our European results.

If we consider what has been amply demonstrated by different investigators, we may safely say the following:

1. The nitriding process, if handled properly, gives surface hardness with practically no distortion.
2. The physical properties of the core material are not changed by nitriding. (Perhaps it is well to mention in passing that the term "Krupp sickness" to indicate temper brittleness seems inappropriate. It is only an act of justice to point out that the firm of Krupp was the first in the world to overcome this difficulty, and, therefore, it seems to me more suitable to use the term "temper brittleness".)
3. The hardness and wear resistance are higher than those of any other steel treating process.
4. The hardness is not injured by tempering temperatures even above 950 degrees Fahr. (500 degrees Cent.).
5. Nitrided parts are free of internal stresses and, therefore, free from ageing effects (important for gages, crankshafts, etc.).
6. Nitrided parts are rust-resisting to a certain extent.
7. The process may be adapted to various applications having varying requirements. This is done by selecting a nitriding steel of the proper composition for each purpose. Fig. 1 gives an idea of the results obtainable by nitriding steels having different compositions.
8. The best results are obtained by quenching and tempering the raw material, and then carrying out the machining and nitriding operations.
9. Various nitriding agents have been tested in the past several years, not only ammonia gas but also cyanides,

sulphocyanates, and so on. Some of them, such as sodium nitrate, failed to give surface hardness; whereas others, such as sodium potassium cyanide, gave good surface hardness but were less easy to handle than ammonia gas.

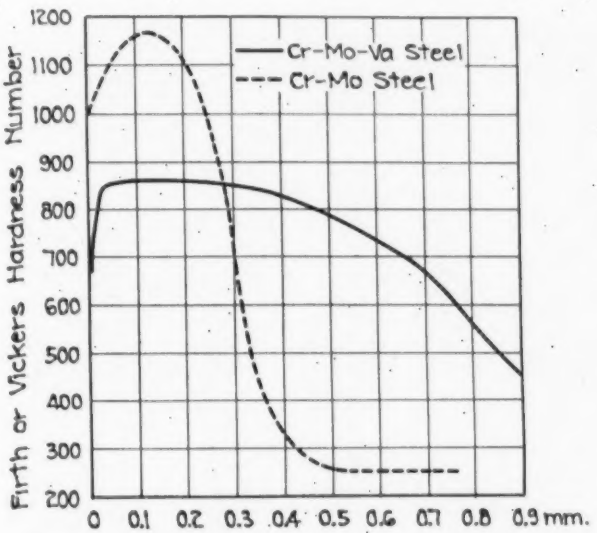


Fig. 1—Hardness-Depth Curves for a Chromium-Molybdenum-Vanadium Steel with 0.22 Per Cent Carbon, 1.5 Per Cent Chromium, 0.4 Per Cent Molybdenum, 0.35 Per Cent Vanadium and for a Chromium-Molybdenum Steel with 0.18 Per Cent Carbon, 3.0 Per Cent Chromium, 0.4 Per Cent Molybdenum.

10. The use of a fan causes circulation and will help to give uniform nitriding.
11. The following conditions should be avoided:
    (a) Surface oxidation.
    (b) Foreign metals touching the steel, such as nickel not yet saturated with nitrogen.
    (c) Foreign substances in the ammonia, such as oil and water.

Returning now to the minor points on which there is not complete agreement, my opinion is as follows:

1. Experiments with higher pressures must be carried out in much more detail before a definite opinion can be expressed as to the effect.
2. Higher nitriding temperatures shorten the time of nitriding but will entail certain disadvantages and may even be dangerous.

(a) Gas dissociation increases, thus reducing the economy.

(b) In consequence of the rapid dissociation at high temperatures, there may be a difference in degree

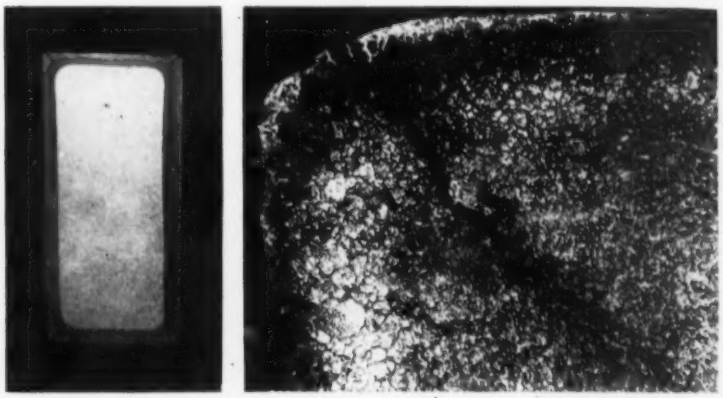


Fig. 2—Photograph Showing the Formation of Hardening Cracks Caused by too High Nitriding Temperature. (1200 Degrees Fahr. 650 Degrees Cent.)

of dissociation at the entrance and the exit of the nitriding box, thus reducing the uniformity of nitriding.

(c) Lifetime of box will be shortened.

(d) The growth of the piece during nitriding will be much greater at high temperatures.

(e) The core hardness may fall.

(f) Since the yield point is very low above 1100 degrees Fahr. (600 degrees Cent.), the pieces may bend or sag above this temperature.

(g) Surface hardness will be much lower when nitriding at high temperatures.

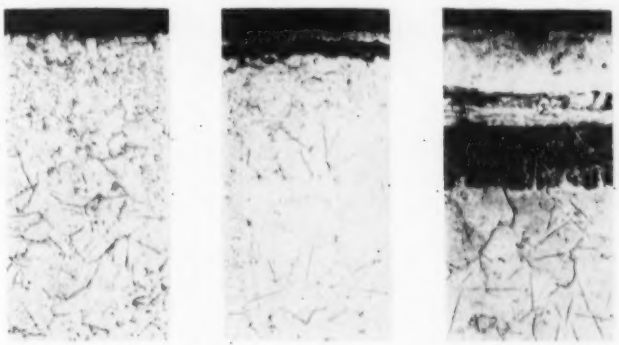
(h) When using high nitriding temperatures, there is a danger of the formation of cracks, which are surely not formed with low nitriding temperatures. Fig. 2 shows a nitrided sample with cracks in the nitrided layer caused by high temperature nitriding. The photomicrograph shows iron nitride in the interior of the crack, thus proving that the cracks were formed before cooling.

I should like to emphasize the view that there should not be

any sacrifice of the best qualities in order merely to save time in nitriding. Although higher temperatures permit more rapid nitriding, the results will not be as good.

THEORY

There has been much progress in recent years, not only in applications but also in research work, as exemplified in the numerous excellent papers presented today. Nevertheless, it must be admitted that we do not as yet have a complete and well substantiated explanation for the hardness obtained by nitriding. Everybody who has worked on these problems knows the difficulties involved, but the solution of these questions would contribute materially to practical progress.



A B C

Fig. 3—Photomicrographs of Low Alloy Steel After Nitriding at Different Temperatures. A, 1020 Degrees Fahr. (550 Degrees Cent.) for 12 Hours. B, 1110 Degrees Fahr. (600 Degrees Cent.) for 10 Hours. C, 1200 Degrees Fahr. (650 Degrees Cent.) for 7 Hours.

Considerable help has been derived by the improvement in hardness testing offered by the Vickers machine. I should like to suggest that all researches be reported in Vickers or Firth figures, which are today the best machines for measuring the hardness of nitrided layers exactly. This would facilitate the exchange of information between different investigators.

The solution of the theoretical problems will call for research along the lines of metallography, chemical analysis, X-ray studies and researches on the effects of alloys on the equilibrium diagram and on the properties of the layers.

May I mention some results that I have obtained in collaboration

with Dr. Hengstenberg, and which may contribute something to our ideas.

1. Chemical and metallographic research has shown that there is a definite difference between nitriding below the eutectoid temperature and nitriding above it, and that this temperature lies between 1070 and 1120 degrees Fahr. (575 and 605 degrees Cent.) for pure iron. Fig. 3 shows the formation of braunite above 1110 degrees Fahr. (600 degrees Cent.). Fig. 4 shows that even with prolonged nitriding at 930 degrees Fahr. (500 degrees Cent.) no braunite layer will be formed, the N-content of which ought to be about 1.5 per cent nitrogen. The microscopical study established this later effect also.

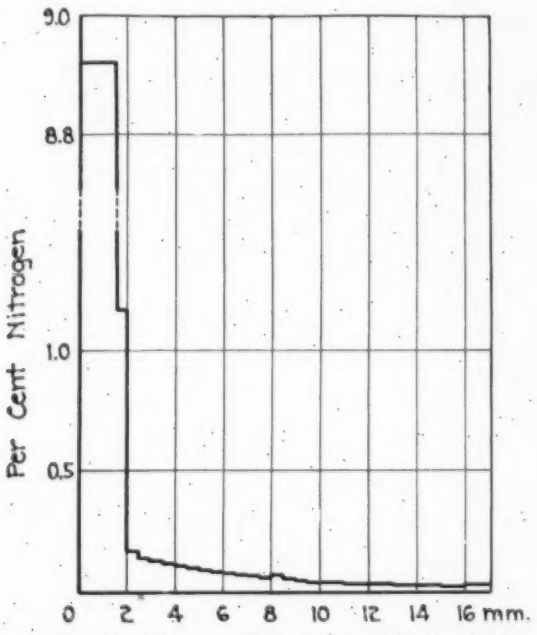


Fig. 4—Nitrogen Content of Mild Steel Nitrided for Several Thousand Hours at 930 Degrees Fahr. (500 Degrees Cent.)

2. This eutectoid temperature is influenced by the presence of alloying elements, as is shown in Fig. 5, for example, for aluminum.
3. Alloy nitrides diffuse extremely slowly in the iron matrix.
4. Nitriding temperature influences the hardness, perhaps, by causing more or less agglomeration of the nitride particles.

   (a) Since nitriding hardness is not affected by even

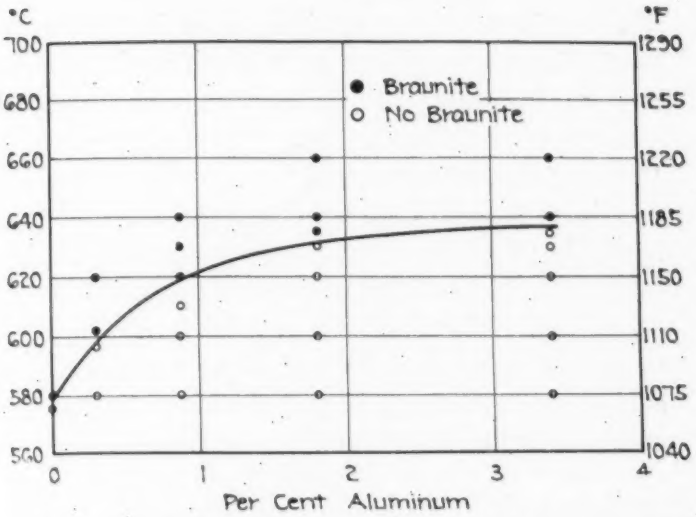


Fig. 5—Curve Showing Change in Eutectoid Temperature with Varying Aluminum Content.

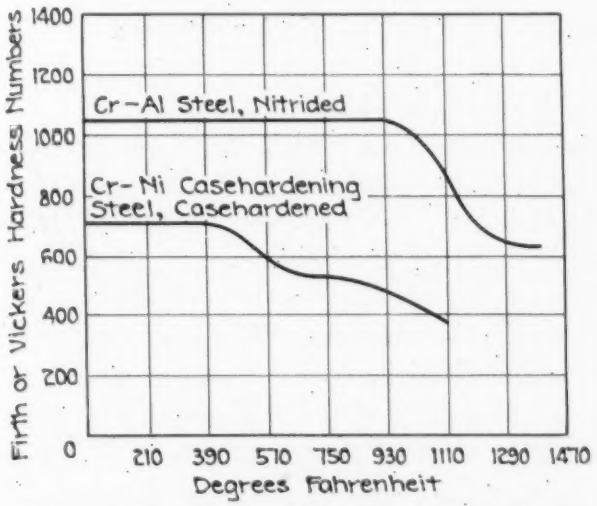


Fig. 6—Curves Showing Influence of Tempering on Hardness of Nitrided Case. Tempering Temperature 210 Degrees Fahr. (100 Degrees Cent.)

prolonged heating at 925 degrees Fahr. (about 500 degrees Cent.), it is clear that agglomeration does not proceed appreciably at this temperature.

(b) Since nitriding at high temperatures, such as 1100 degrees Fahr. (600 degrees Cent.), gives lower hardness, it may be concluded from the theoretical considerations in item 6 below that agglomeration proceeds at this temperature.

5. The hardness of the nitrided layer is not to be attributed to the hardness of the alloy nitrides themselves. It may well be, however, that the hardness of these particles contributes to wear resistance.
6. With all due reservations, it may still be suggested with a certain amount of assurance that the mechanism of nitrogen hardening bears a resemblance to the quench-hardening of steels, insofar as both seem to be caused by space lattice distortion. We need not say here whether we subscribe to the theory of Jeffries and Archer, or to that of Maurer, since in the last analysis both theories rest on considerations of space-lattice distortion.

Now as to practical problems.

We are still faced with the following tasks:

1. Getting more experience in choosing the best kind of nitriding steel for each particular purpose.
2. Machining of nitriding steels with high core strength without leaving machining stresses.
3. Finding steels in which the preliminary quenching and tempering leaves almost no residual stresses.
4. Obtaining welds in which the weld junction will be perfectly hard after nitriding.
5. Making drop forgings and hot pressed pieces free of surface oxidation, which would otherwise cause inferior quality of the nitrided layer.
6. Further research in the nitriding of cast iron.
7. Study of other nitriding agents, including catalyzers.

And now in conclusion, may I express my appreciation for the opportunity of appearing before you, and the hope that this process and your researches will contribute to progress in American machine design. I wish to express my sincere thanks to M. A. Grossmann, who very kindly helped me in transcribing this address.

RESEARCHES ON NITRIDING STEELS

By Oscar E. Harder, James T. Gow and Lowell A. Willey

Abstract

The work reported in this paper may be divided into two parts. In Part I a study was made of a considerable number of steels to determine their suitability for nitriding. Nitriding temperatures used were 875 and 1000 degrees Fahr. The hardnesses obtained were determined by means of the Rockwell and Shore instruments, the latter being used more extensively. The results obtained on these steels are shown in tables and graphs. In Part II more particular attention was given to the effect of nitriding temperature, rate of gas flow, gas decomposition, etc., on the character of the nitrided case. Hardness values were determined by the Vickers instrument. The steels studied include chromium-aluminum, a chrome-vanadium steel of S. A. E. 6135 type, and a chrome-nickel-molybdenum steel. The nitriding temperatures included 875, 975, 1075, and 1175 degrees Fahr. The results obtained are shown in tables and graphs. In general, increasing the nitriding temperature was found to increase the depth of penetration, but for temperatures higher than 975 generally decreases the hardness of the case. The nitriding operation was found to remove carbon from steel, the amount of carbon removed increasing with the temperature of nitriding. The chromium-aluminum steel was found to produce a higher surface hardness than either of the other steels studied.

THE work reported in this paper has been in progress over a period of two years and may be divided into two parts. The first part covers work done in 1927-28 and has to do with a rather preliminary examination of a large number of steels with reference to their suitability for nitriding. In this connection a study was

Of the authors, members of the society, Dr. O. E. Harder is professor of metallography, School of Mines and Metallurgy, University of Minnesota, Minneapolis, Minnesota; James T. Gow, graduate student in metallography, Minnesota School of Mines and Metallurgy, '27-28, instructor in chemical engineering, Purdue University, 1928-29, and Lowell A. Willey, metallurgical engineer degree, Minnesota School of Mines and Metallurgy, 1929, is now in metallographic laboratory of Aluminum Company of America, New Kensington, Pa. Manuscript received June 25, 1929.

made of the effect of the condition of the steel at the time it was nitrided and the resulting properties, and two nitriding temperatures, 875 and 1000 degrees Fahr. (470 and 540 degrees Cent.), were used. The cases were examined microscopically and tested for hardness, using the Rockwell and scleroscope instruments.

The second part of the work was carried out during 1928-29 and had to do more with the effect of nitriding temperature, effect of rate of gas flow and gas decomposition on the properties of nitrided cases. The hardness of the cases has been determined by means of the Vicker's hardness tester, which seems to be more satisfactory than the Rockwell or scleroscope instruments.

No attempt will be made in this paper to review the literature or to give a comprehensive bibliography because it is understood that another author will deal especially with these subjects at this session on nitriding.

Part I—Steels For Nitriding

The steels used in this investigation were selected from standard commercial products which were thought to have possibilities for nitriding, and some special steels which were supplied by one of the steel manufacturers. The laboratory numbers for these steels, their types, and actual or typical analyses are given in Table I.

Table I
Chemical Compositions of Steels Used in Part I

Lab. No.	Types of Steels	Chemical Composition								
		C	Mn	Si	Ni	Cr	Mo	V	Al	W
9	W	0.50	0.22	0.14	....	....	....	....	....	1.07
36	Cr-Si	0.44	0.80	0.47	....	0.78	....	....	....	....
72	Ni	0.29	0.50	0.06	3.58	....	....	....	....	....
76	C-Fe	1.18	0.56	0.11	....	....	....	....	....	....
94	Cr-V	0.35	0.70	0.18	....	0.89	....	0.19	....	....
100	Cr-Mo	0.25	0.63	0.10	....	0.91	0.28	....	....	....
129	Cr-Ni	0.30	0.63	0.20	1.25	0.65	....	....	....	....
133	Cr	0.31	0.71	0.18	....	1.03	....	....	....	....
134	Cr	0.38	0.77	0.20	....	1.03	....	....	....	....
141	Ni-Mo	0.12	0.38	0.20	1.57	....	0.24	....	....	....
145	Mn	0.40	0.90	....	0.20	0.20	....	....	....	....
150	Cast iron	3.42	0.77	1.87	....	....	....	....	....	....
152A	Cr-Al	0.44	0.50	0.34	....	1.61	....	....	0.84	....
152C	Cr-Al	0.09	0.76	0.28	....	1.47	....	....	1.01	....
152D	Cr-Ni-Al	0.33	0.68	0.21	1.39	1.58	....	....	1.30	....
153	Ingot iron	....	....	....	....	....	....	....	....	....
155	C-V	0.52	0.49	0.21	....	....	....	0.19	....	....
156	C-V-Si	0.18	0.71	0.60	....	0.03	....	0.15	....	....
157	Ni-V	0.23	0.91	0.39	1.55	....	....	0.11	....	....
158	C-V-Si	0.55	0.48	0.64	....	....	....	0.15	....	....
159	C-V-Si	0.14	0.63	1.25	....	....	....	0.24	....	....
160	C-V-Si	0.25	0.88	1.95	....	0.10	....	0.19	....	....
161	C-V-Si	0.36	0.58	1.58	....	....	....	0.14	....	....
162	Cr-Ni-V	0.36	0.83	0.07	2.15	1.07	0.08	0.25	....	....
163A	C-Mo	0.44	0.57	0.15	....	....	0.19	....	....	....

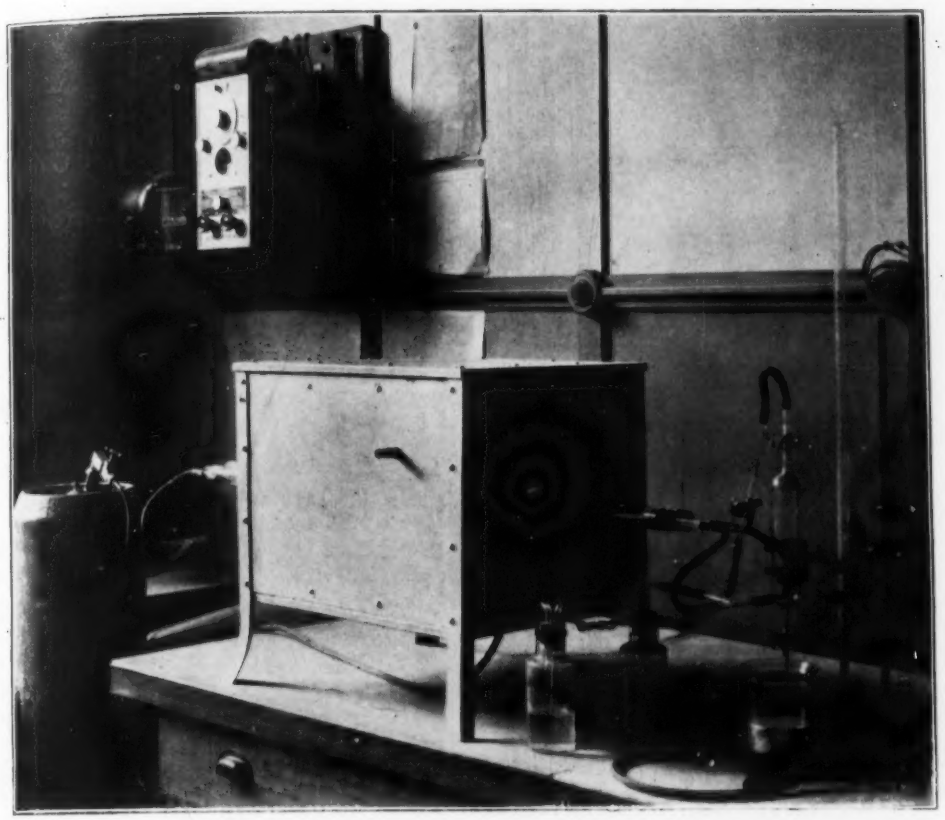


Fig. 1—Nitriding Apparatus.

Apparatus Used.—The apparatus used in this investigation for nitriding is shown in Fig. 1. The nitriding tubes are approximately 1 inch inside diameter, the furnace was electrically heated and the temperature was automatically controlled.

Experimental Work in Part I.—The outline of the experimental work conducted in connection with Part I of this research is shown in Table II.

Results of Tests on Series No. 1.—Microscopic examination of the steel before nitriding showed that the steels were all in the annealed condition. The chromium-aluminum steel 152A was largely pearlitic while steel 152D and 152C were mostly spheroidized cementite or granular pearlite as it is sometimes called. The chromium-molybdenum, chromium-nickel, and chromium steels were partially spheroidized pearlite.

The microstructure of the nitrided cases of these steels are shown in Figs. 2 to 7. Figs 2 to 4 show the tendency of the chro-

Table II
Outline of Experimental Work in Part I

Series No. 1.
Steels Nos. 100, 129, 133, 152A, 152C and 152D nitrided in the "as received" condition 49 hours at 875 degrees Fahr. (470 degrees Cent.).

Series No. 2.
Steels Nos. 72, 76, 134, 145, and 152D nitrided in the "as received" condition 90 hours at 875 degrees Fahr. (470 degrees Cent.).

Series No. 3.
Steel No. 100 (S.A.E. 4125) nitrided in quenched and tempered condition (tempered at 870-1200 degrees Fahr.) for 90 hours at 875 degrees Fahr.

Series No. 4.
Steels Nos. 36, 72, 94, 100, 129, 134, 141, 145, 152A, 152C, and 153 nitrided in the quenched and tempered condition (tempered 2.5 hours at 1110 degrees Fahr.) 90 hours at 1000 degrees Fahr.

Series No. 5.
Steels Nos. 152D, 155, 156, 157, 158, 159, 161, 162, and 163A nitrided in the quenched and tempered condition (tempered 3 hours at 1110 degrees Fahr.) for 90 hours at 1000 degrees Fahr.

mium-aluminum steels to form a porous, more or less brittle case near the surface. This tendency is more pronounced in the case of steel 152C, and this will be discussed more later. In the case of the chromium-aluminum steel 152C the nitride seems to form in pearlitic patches while in steels 152A and 152D there is apparently a solid solution with some rejection to grain boundaries. Figs. 5, 6, and 7 show some tendencies to porosity of the case in these steels but it is less pronounced in the case of the chromium-aluminum steels, particularly steel 152C. In all of these steels there was an apparent decrease in the amount of carbide during the nitriding operation.

The increase in hardness and depth of case of the steels are shown in Table III. Unfortunately, these hardness tests were made with the Rockwell instrument and are not readily comparable with other data.

Table III
Effect of Nitriding 49 Hours at 875 degrees Fahr. (470 degrees Cent.) on Hardness and Depth of Case

Lab. No.	Types of Steel	Rockwell Hardness (B Scale) Case	Original	Increase in Hardness	Depth of Case (Inch)
152A	Cr-Al	112.35	95.2	17.2	0.025
152C	Cr-Al	118.15	74.2	44.0	0.030
152D	Cr-Ni-Al	114.22	95.6	19.6	0.030
100	Cr-Mo	115.16	89.0	26.2	0.020
133	Cr	107.63	84.4	20.0	0.030
129	Cr-Ni	104.85	84.4	20.4	0.025

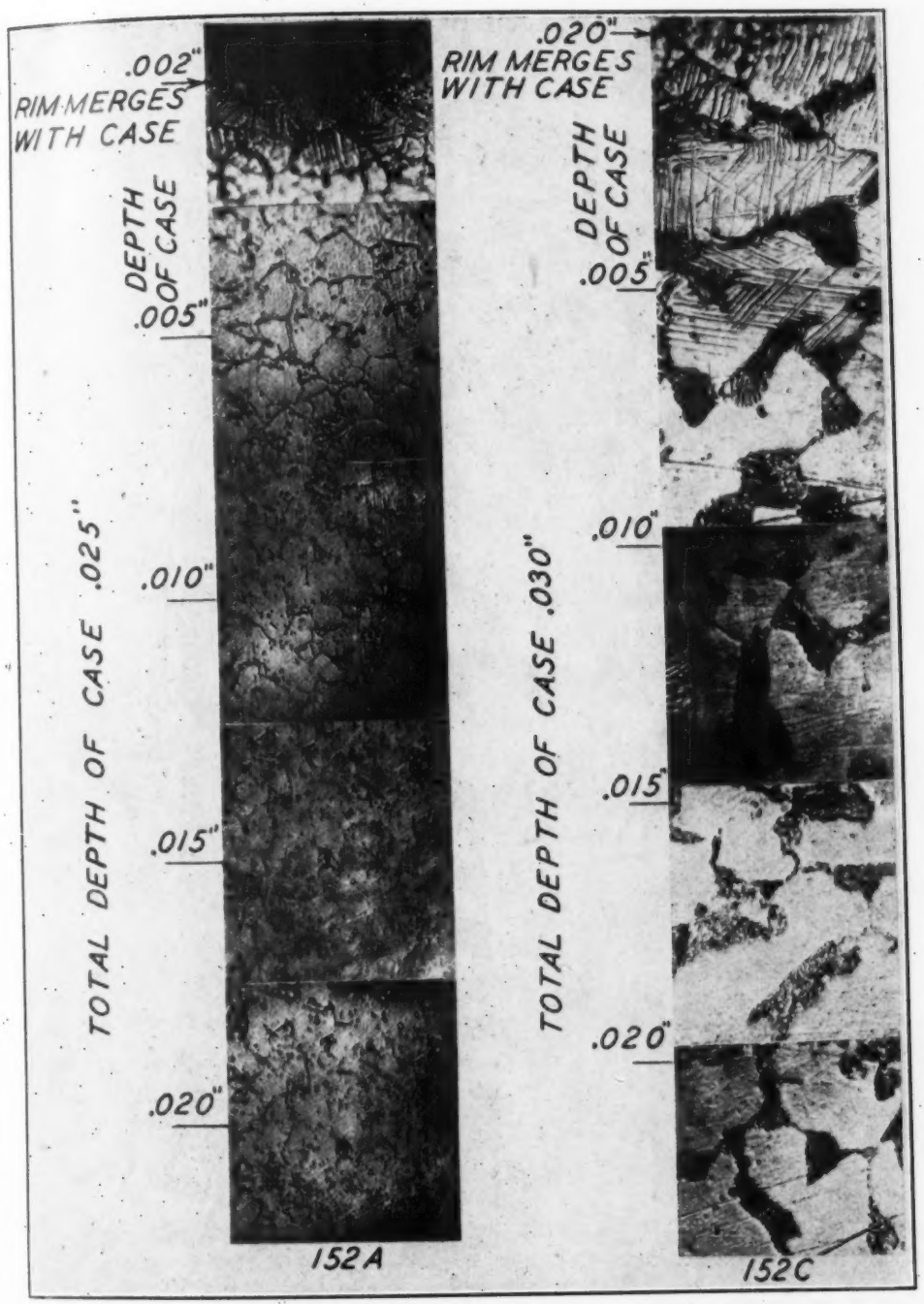


Fig. 2—Microstructure of Case of Chromium-aluminum Steel 152A, Nitrided 49 hours at 875 Degrees Fahr. (470 Degrees Cent.) × 500.

Fig. 3—Microstructure of Case of Chromium-aluminum Steel 152C, Nitrided 49 hours at 875 Degrees Fahr. (470 Degrees Cent.) × 500.

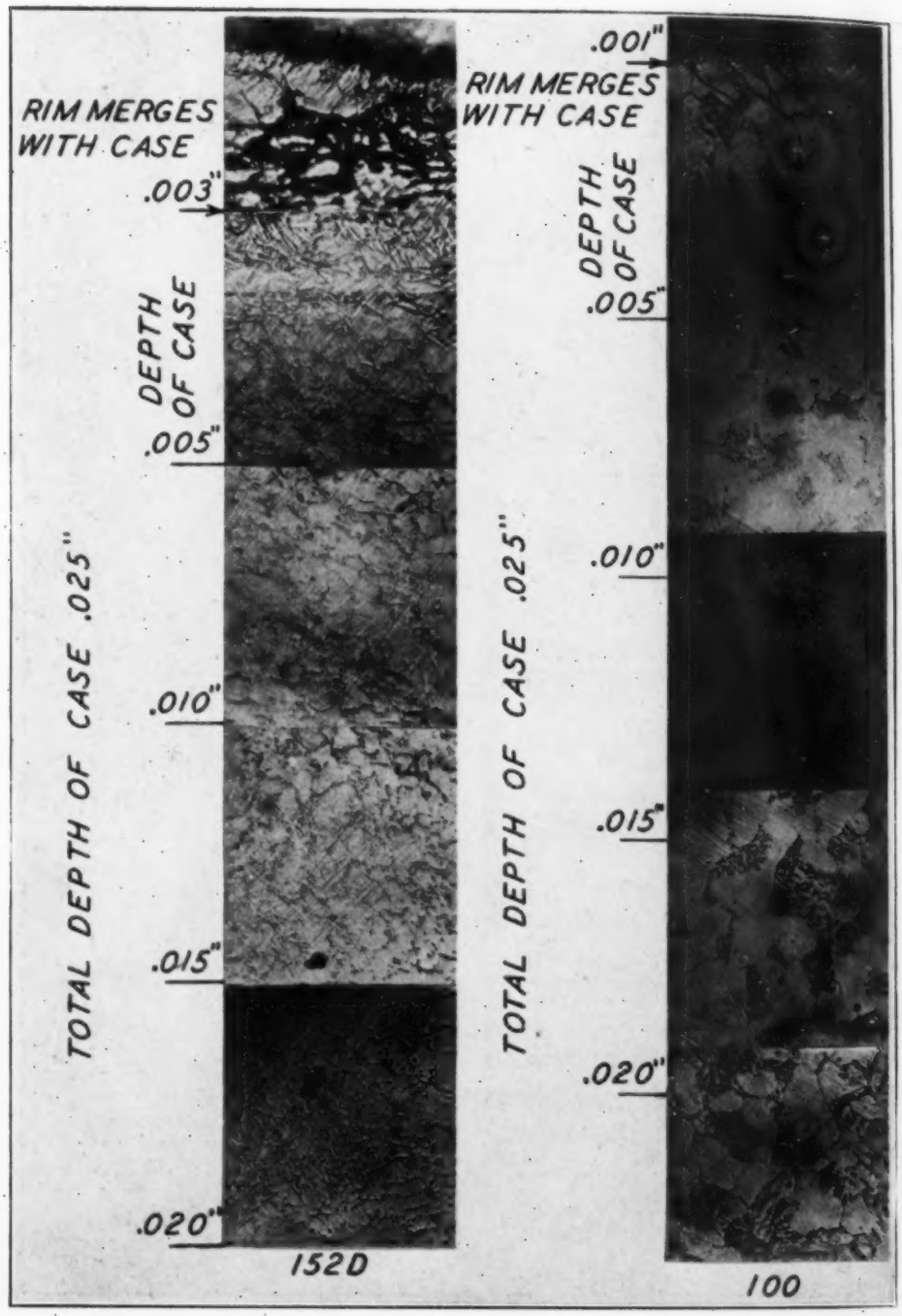


Fig. 4—Microstructure of Case of Chromium-nickel-aluminum Steel 152D, Nitrided 49 hours at 875 Degrees Fahr. (470 Degrees Cent.) × 500.

Fig. 5—Microstructure of Case of Chromium-molybdenum Steel, Nitrided 49 hours at 875 Degrees Fahr. (470 Degrees Cent.) × 500.

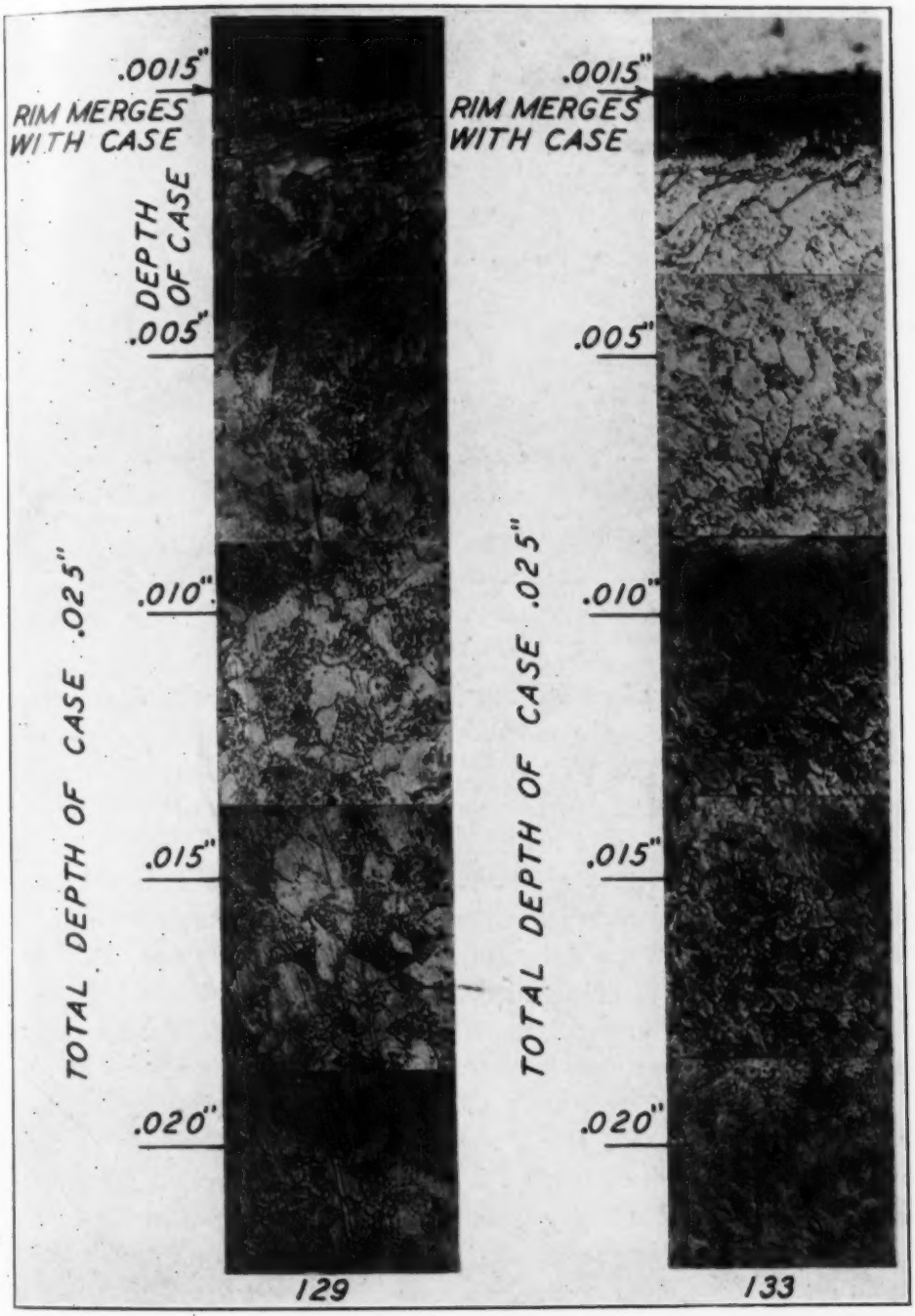


Fig. 6—Microstructure of Case of Nickel-chromium Steel, Nitrided 49 hours at 875 Degrees Fahr. (470 Degrees Cent.) × 500.

Fig. 7—Microstructure of Case of Carbon-chromium Steel, Nitrided 49 hours at 875 Degrees Fahr. (470 Degrees Cent.) × 500.

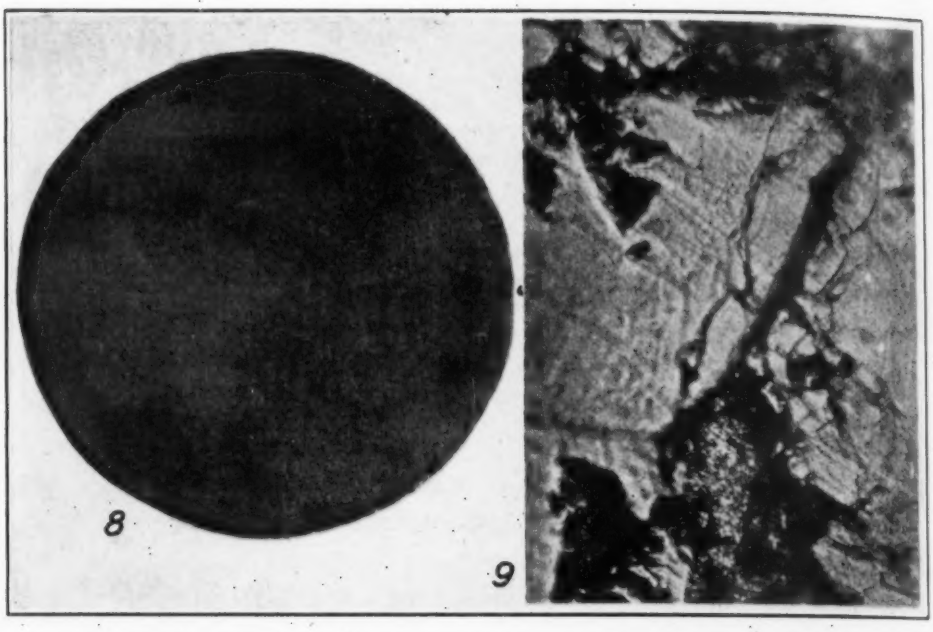


Fig. 8—Porous Rim on Nitrided Specimen of Chromium-aluminum Steel 152C × 2.5
Fig 9—Photomicrograph of Porous Rim, Chromium-aluminum Steel 152C. × 1000.

The porous rim around a sample of the chromium-aluminum steel 152C is shown at a slight magnification in Fig. 8 and the detail of this porous structure is shown in Fig. 9. In this photomicrograph the light areas appear to be the usual hard nitride product while the dark areas are porous and brittle.

Discussion of Results of Series No. 2.—Since Series 1 had shown that in addition to the chromium-aluminum steels such alloy steels as chromium-molybdenum, nickel-chromium, and straight chromium steels could be nitrided, it was considered desirable to determine if nickel, manganese, ingot iron, and high carbon steels could be nitrided. For purposes of comparison a chromium steel and a chromium-aluminum steel were included. It was found on microscopic examination that there was practically no nitriding of the ingot iron or the high carbon steel. The straight nickel steel and the manganese steel showed very little nitriding. The depth of the cases on the nickel and manganese steels was only about one-fourth that found on the chromium steel.

There was found to be some reaction between the nitriding gases and the white cast iron. It, therefore, appeared that the presence of carbide is necessary for success in nitriding and that the carbides of iron alone are not active and the addition of those alloying elements

which go primarily into the ferrite is not beneficial to the nitriding operation.

Discussion of Results of Series No. 3.—The tests included in Series 3 were made for the purpose of determining the effect of carbide dispersion or the size of carbide particles on the nitriding treatment. The steel used was a chromium-molybdenum, No. 100, and the heat treatment, microstructure, and hardness of the case are given in Table IV.

Table IV

Effect of Carbide Dispersion on Hardness of Nitrided Case of Chromium-Molybdenum Steel

Series 3, Nitrided 90 hours at 875 degrees Fahr. (470 degrees Cent.)

Specimen No:	Heat Treatment	Microstructure	Rockwell hardness of case. B scale.
1	Furnace-cooled	Pearlitic	115
2	Air-cooled	Sorbito-pearlitic	116
3	Water-quenched	Martensitic	121
4	Water-quenched and tempered at 870°F.	Sorbitic	120
5	Water-quenched and tempered at 1000°F.	Sorbitic	120.5
6	Water-quenched and tempered at 1200°F.	Spheroidized	116

The results show that increased hardness was obtained by using those steels which had the carbide particles in the finely divided condition such as is obtained by quenching or by quenching followed by tempering. Since the best physical properties of the core would be obtained by quenching followed by tempering to produce machinability in commercial practice, it seemed advisable to use some such treatment in this experimental work. For that reason the steels used in Series 4 and 5 were first hardened by quenching in water followed by tempering 2 to 3 hours at 1110 degrees Fahr. (600 degrees Cent.).

Discussion of Results of Series 4 and 5.—In conformity with the best indicated practice from previous tests, the steels included in these two series were first quenched and then tempered at 1110 degrees Fahr. (600 degrees Cent.) before nitriding. The steels which were included in these two series and the resulting hardness of the cases at different depths are shown in Table V.

An attempt has been made to show the effects of a number of alloying elements on the hardness and depth of case by plotting the values obtained for the different kinds of steel and by arranging steels containing one principal element on a single sheet; for example, steels which contain nickel are shown in Fig. 10, the chromium steels

Table V

Hardness and Depth of Case of Steels Nitrided 90 Hours at 1000 Deg. Fahr.

Series 4 and 5; specimens quenched and tempered at 1110 Degrees Fahr. before nitriding

Depth of Case		.000	.002	.005	.010	.015	.020	.030	.040	.050	.060"
Lab. No. and Type of Steel		Scleroscope Hardness									
36	Cr-Si	64	62	58	53	50	45	45	..	..	..
72	Ni	37	44	42	42	..	42	42	41	..	..
94	Cr-V	71	78	74	70	66	59	52	48	45	45
100	Cr-Mo	66	72	72	68	64	61	60	58	52	48
129	Cr-Ni	66	63	56	48	47	45	43	43	..	..
134	Cr	60	67	67	63	58	58	53	42	47	..
141	Ni-Mo	65	68	66	63	59	57	54	50	47	..
145	Mn	61	57	57	57	54	55	53	48	..	..
152A	Cr-Al	75	98	94	86	67	57	46	44	41	..
152D	Cr-Ni-Al	78	94	90	88	87	79	54	46	46	..
155	C-V	63	61	60	61	58	56	53	53	53	..
156	C-V-Si	62	62	62	63	58	55	52	47	44	..
157	Ni-V	57	..	60	58	58	55	53	50	48	..
158	C-V-Si	57	60	61	60	59	57	55	..	..	..
159	C-V-Si	70	72	70	69	68	58	51	..	..	..
160	C-V-Si	78	75	68	64	58	53	47	42	..	..
161	C-V-Si	67	63	59	57	54	50	43	42	40	..
162	Cr-Ni-V	70	78	79	73	71	68	62	60	57	54
163A	C-Mo	59	60	60	58	54	53	52	52	52	..

in Fig. 11, the molybdenum steels in Fig. 12 and the vanadium steels in Fig. 13.

The first conclusion which is very evident is that plain nickel steels are not hardened to any appreciable extent or depth by nitriding. The addition of chromium, vanadium, or molybdenum materially improves the nitriding properties, molybdenum giving greater depth of case and the molybdenum apparently giving the best properties. The addition of both chromium and vanadium produces a case of fair hardness with greater depth than the chromium-nickel-aluminum steel 152D. The addition of chromium and aluminum, as in steel 152D, produced the greatest hardness with a greater depth of case than was obtained with the chromium-aluminum alloy, that is steel 152A. It, therefore, appears that nickel alone does not give the steel nitriding properties, but that nickel may have a beneficial effect when used with other alloying elements such as chromium, vanadium, molybdenum and aluminum. The indications are that it favors depth of penetration.

In the case of chromium steels (Fig. 11), the plain chromium steel seems to be superior to chromium-silicon or chromium-nickel. On the other hand, chromium-molybdenum, chromium-vanadium, and chromium-aluminum gave better results than the straight chromium steel, the chromium-aluminum giving the highest hardness obtained.

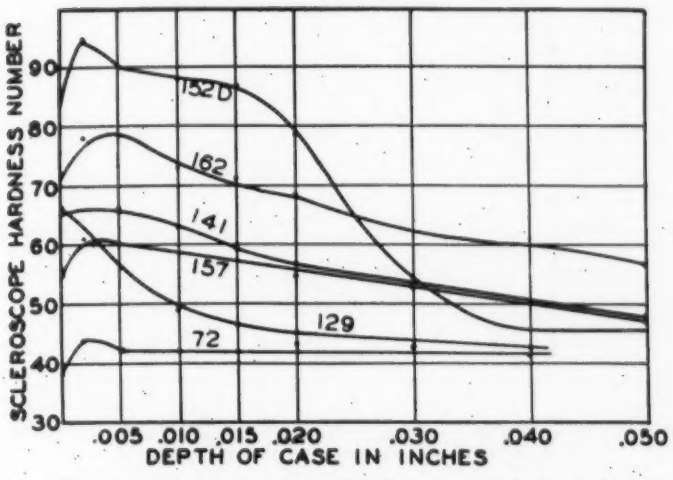


Fig. 10—Hardness of Nitrided Cases on Nickel and Nickel-containing Steels.

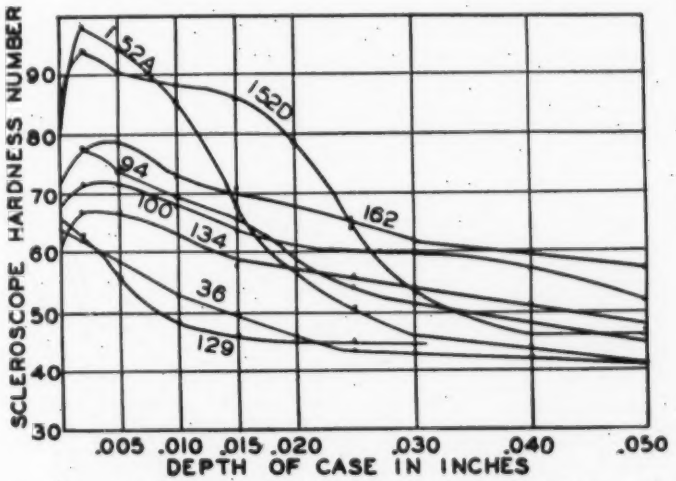


Fig. 11—Hardness of Nitrided Cases on Chromium and Chromium-containing Steels.

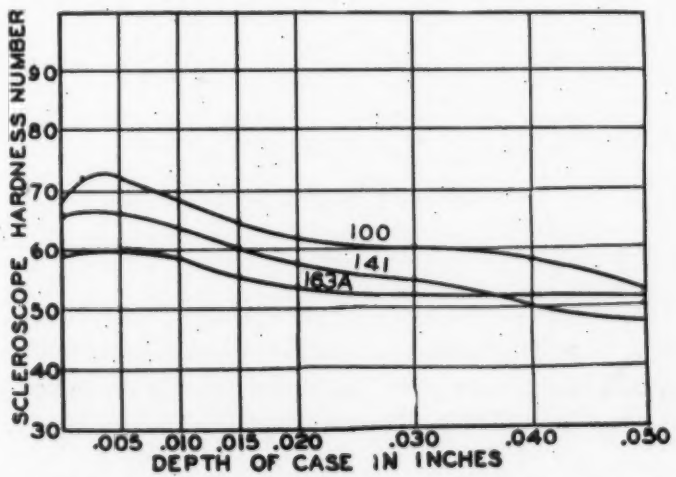


Fig. 12—Hardness of Nitrided Cases on Molybdenum and Molybdenum-containing Steels.

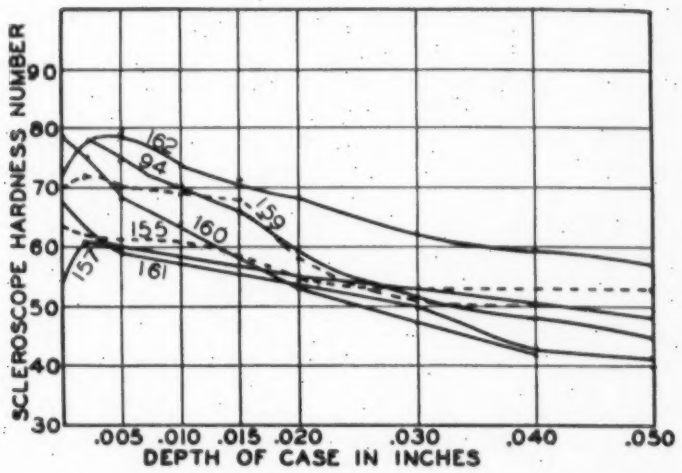


Fig. 13—Hardness of Nitrided Cases on Vanadium and Vanadium-containing Steels.

More complex steels, chromium-vanadium-nickel and chromium-nickel-aluminum were also superior to straight chromium steel, the chromium-nickel-aluminum being notable for hardness and depth of

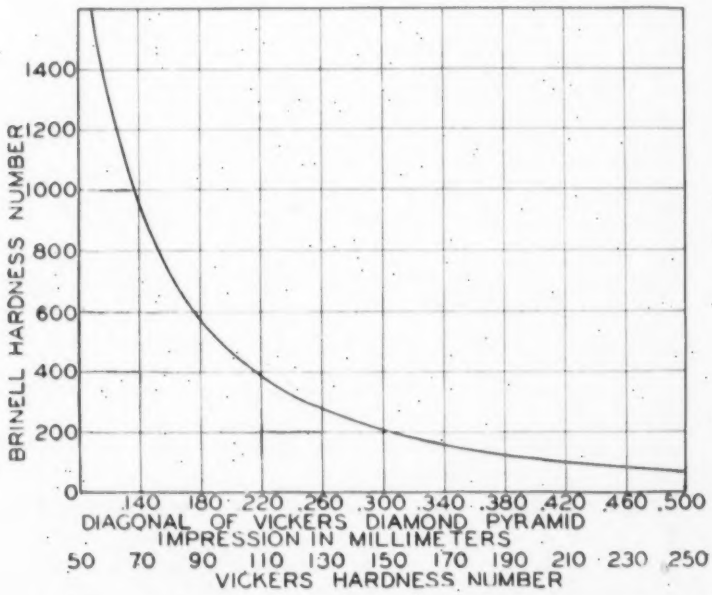


Fig. 14—Relation of Brinell Hardness Number to Diagonal of Vickers Diamond Pyramid Impression.

case. These results indicate that nickel and silicon have a harmful effect as additional elements to chromium steels, but that molybdenum, vanadium and aluminum have beneficial effects and even nickel with vanadium may be added to chromium steels to advantage.

The results for the molybdenum steels are shown in Fig. 12. We observed that these steels show only medium hard cases but that there is a considerable depth of penetration. Nickel when added to molybdenum seems to improve the case but the addition of chromium is more beneficial. The possibility of further improving alloys of this type with further alloying looks promising.

The vanadium steels are shown in Fig. 13. Vanadium gives comparatively low hardness in the case but considerable depth of penetration. The addition of nickel, as in steel 157, does not improve the straight vanadium steel. The addition of chromium seems to be beneficial but the best results are obtained by addition of both chromium and nickel. The effect of silicon seems to be slightly beneficial in this case, steels Nos. 159 and 160, although it had been found to have a harmful effect on chromium steels.

These conclusions must be considered preliminary because in no case have all other variables been kept constant when new alloying elements have been added to study the effect on the case; they are, however, suggestive of the relations which obtain.

Part II.—Effect of Nitriding Temperature, Rate of Gas Flow and Gas Decomposition

In this part of the investigation a study has been made of the effect of three different rates of gas flow at four different temperatures on the per cent of gas decomposition, the hardness of the case, the depth of case produced, and the increase in weight due to nitriding. The steels used in this investigation are shown in Table VI.

Table VI
Chemical Composition of Steels Used in Part II

Element	Steel 152A	Chromium-Vanadium	Chromium-Nickel-Molybdenum
Carbon	0.44	0.35	0.35 to 0.45
Manganese	0.50	0.70	0.50 to 0.80
Phosphorus	0.014	0.013	0.03 maximum
Sulphur	0.02	0.029	0.03 maximum
Silicon	0.34	0.18	.....
Chromium	1.61	0.89	0.45 to 0.75
Aluminum	0.84	....	.....
Vanadium	....	0.19	.....
Molybdenum	....	....	0.30 to 0.40
Nickel	....	....	1.50 to 2.00

These tests were made in three series in which the rate of gas flow varied in the following approximate ratios, 1 : 6 :18. As would be expected, the amount of gas decomposition decreased as the rate of

Table VII

Relation of Temperature, Gas Decomposition and Heat Treatment to Properties of Nitrided Cases

Number	Type of Steel	Condition of steel	Nitriding Temp. °F.	Per cent NH_3 dissociated	Incr. in wt. mgms. per sq. in.	Surface	Brinell Hardness Number Inches below surface .005	.010	.015	.020	.025	.030	.035	.040	.045	Depth of case
152A-1	Cr-Al	An.	875	1.5	18.2	919	523	245	212	197	187	178	167	171	168	.015"
152A-25	Cr-Al	An.	875	7.0	14.6	932	369	227	217	201	189	181	177	175	173	.015
152A-26T	Cr-Al	Temp.	875	7.0	16.8	1097	362	233	220	198	200	197	195	197	192	.009
152A-29	Cr-Al	An.	875	16.0	11.8	932	359	227	205	203	195	189	183	178	176	.010
152A-30T	Cr-Al	Temp.	875	16.0	16.8	1150	398	240	230	213	203	206	206	206	203	.009
152A-5	Cr-Al	An .	975	11.0	32.7	945	836	278	211	193	191	178	177	173	173	.014
152A-21	Cr-Al	An.	975	19.0	26.3	973	530	247	217	206	201	183	176	176	175	.015
152A-22T	Cr-Al	Temp.	975	19.0	29.0	1015	773	306	239	217	213	211	206	211	210	.013
152A-31	Cr-Al	An.	975	34.0	29.6	1033	734	268	225	201	188	183	183	180	178	.016
152A-32T	Cr-Al	Temp.	975	34.0	33.2	1015	814	379	264	217	209	210	206	216	203	.016
152A-13	Cr-Al	An.	1075	36.0	55.5	698	541	483	458	230	178	170	167	163	163	.021
152A-23	Cr-Al	An.	1075	49.0	40.0	753	651	548	341	195	188	176	170	171	173	.019
152A-24T	Cr-Al	Temp.	1075	49.0	45.1	871	691	584	497	258	217	217	216	213	213	.020
152A-33	Cr-Al	An.	1075	55.0	34.8	783	612	497	220	178	175	176	173	176	173	.025
152A-34T	Cr-Al	Temp.	1075	55.0	47.8	848	635	572	501	332	216	206	201	198	201	.023
152A-9	Cr-Al	An.	1175	74.0	64.2	473	473	429	366	353	335	296	177	170	167	.033
152A-27	Cr-Al	An.	1175	78.0	59.4	536	409	409	416	398	347	191	173	176	172	.029
152A-28T	Cr-Al	Temp.	1175	78.0	53.1	542	497	429	425	412	309	191	180	181	181	.028
152A-35	Cr-Al	An.	1175	84.0	51.4	542	469	451	409	394	314	198	189	180	180	.022
152A-36T	Cr-Al	Temp.	1175	84.0	56.9	651	482	473	469	446	409	324	210	192	188	.033
163-3	Cr-Ni-Mo	Temp.	875	7.0	5.7	433	309	268	258	256	247	243	239	247	242	.011
163-5	Cr-Ni-Mo	Temp.	875	16.0	5.0	427	402	294	276	270	266	268	260	256	258	.012
163-1	Cr-Ni-Mo	Temp.	975	19.0	11.7	507	376	324	321	306	289	285	285	280	276	.021
163-6	Cr-Ni-Mo	Temp.	975	34.0	9.9	455	359	324	296	287	276	264	260	258	247	.027
163-2	Cr-Ni-Mo	Temp.	1075	49.0	18.6	376	347	338	335	311	306	289	280	266	258	.032
163-7	Cr-Ni-Mo	Temp.	1075	55.0	19.3	347	324	324	330	309	296	285	260	260	250	.033
163-4	Cr-Ni-Mo	Temp.	1175	78.0	28.5	296	294	276	274	274	270	266	256	252	243	.023
163-8	Cr-Ni-Mo	Temp.	1175	84.0	24.4	309	280	294	296	289	274	266	264	268	260	.021
94-5	Cr-V	Temp.	875	7.0	7.7	584	359	268	240	227	211	216	210	209	203	.021
94-7	Cr-V	Temp.	875	16.0	6.6	523	425	319	266	343	235	235	235	225	222	.019
94-3	Cr-V	Temp.	975	19.0	12.7	591	584	497	343	266	258	243	240	240	235	.025
94-8	Cr-V	Temp.	975	34.0	12.2	530	482	473	425	204	252	242	232	220	213	.034
94-4	Cr-V	Temp.	1075	49.0	19.5	464	478	425	390	347	319	299	268	266	249	.034
94-9	Cr-V	Temp.	1075	55.0	25.5	455	460	409	390	359	324	311	289	264	242	.040
94-6	Cr-V	Temp.	1175	78.0	30.2	386	332	289	266	266	260	260	249	242	327	.035
94-10	Cr-V	Temp.	1175	84.0	31.5	366	332	319	301	289	289	296	285	276	266	.032

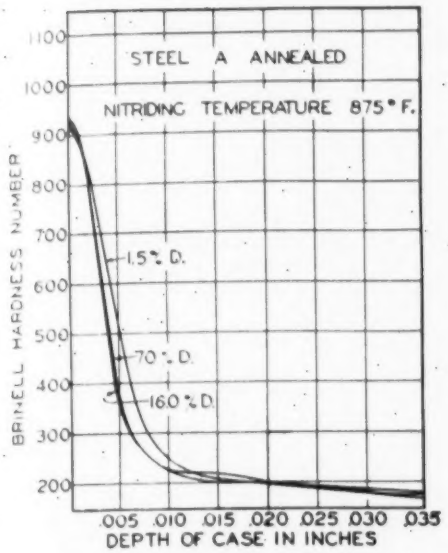


Fig. 15—Effect of Dissociation on Hardness of Case. Chromium-aluminum Steel 152A, Annealed. Nitrided at 875 Degrees Fahr. (470 Degrees Cent.).

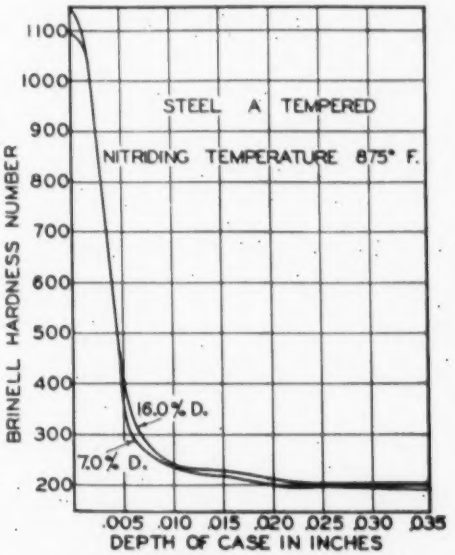


Fig. 16—Effect of Dissociation on Hardness of Case. Chromium-aluminum Steel 152A, Tempered. Nitrided at 875 Degrees Fahr. (470 Degrees Cent.).

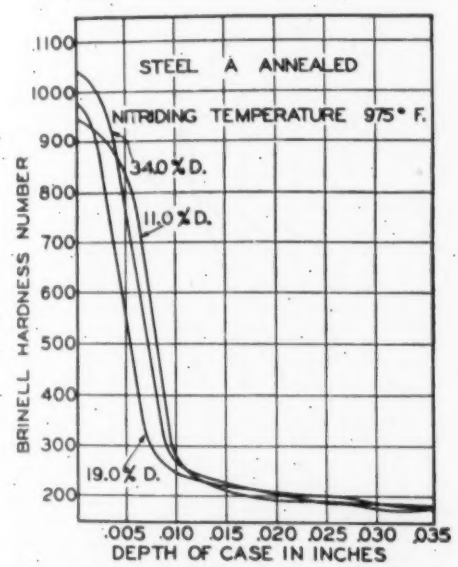


Fig. 17—Effect of Dissociation on Hardness of Case. Chromium-aluminum Steel 152A, Annealed. Nitrided at 975 Degrees Fahr. (525 Degrees Cent.).

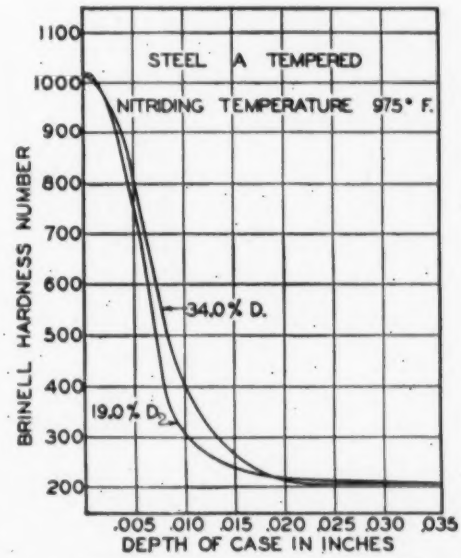


Fig. 18—Effect of Dissociation on Hardness of Case. Chromium-aluminum Steel 152A, Tempered. Nitrided at 975 Degrees Fahr. (525 Degrees Cent.).

gas flow increased. This relation makes it possible in comparing different series to tell at a glance the relative rate of gas flow.

The specimens used in these tests were generally one-half inch square by 1½ to 2 inches in length. The specimens were taper-ground and polished after nitriding so that the tests at distances of

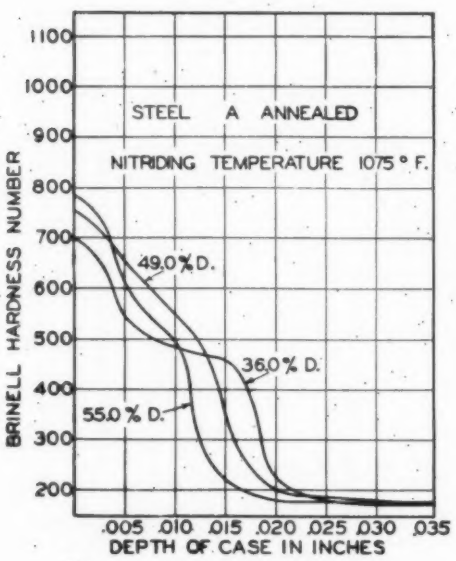


Fig. 19—Effect of Dissociation on Hardness of Case. Chromium-aluminum Steel 152A, Annealed. Nitrided at 1075 Degrees Fahr. (580 Degrees Cent.).

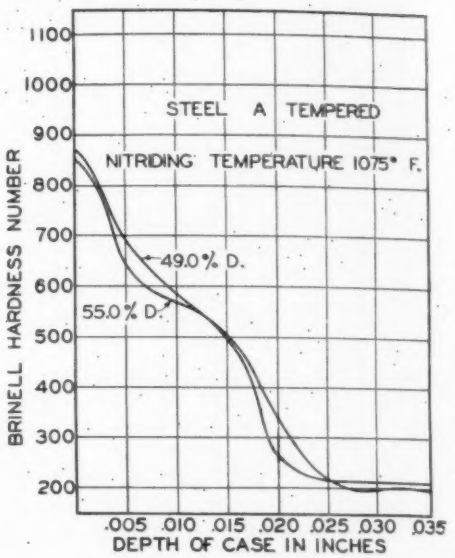


Fig. 20—Effect of Dissociation on Hardness of Case. Chromium-aluminum Steel 152A, Tempered. Nitrided at 1075 Degrees Fahr. (580 Degrees Cent.).

$\frac{1}{10}$ inch along the specimen represented a difference in case depth of 0.005 inch.

Brinell hardness numbers were obtained by means of the Vickers diamond pyramid, using a 10-kilogram load applied for 30 seconds. The relation between the diagonals of the Vickers diamond pyramid impressions and the Brinell hardness numbers is shown in Fig. 14. This curve was drawn from theoretical considerations of the relation between the surface of the impression and the load applied. The authors are indebted to Mr. G. M. Eaton for suggestions in connection with the hardness testing.

Results of Tests.—Table VII shows the different steels which were used in this test, the condition of the steels, the nitriding temperature, gas dissociation, increase in weight, hardness at different depths of case, and, finally, depth of case. The depth of case was arbitrarily taken as that depth at which there was an increase of 25 per cent over the hardness of the core.

Effect of Moisture on Case.—Nitriding tests were made on chromium-aluminum steel 152A at 875, 975, 1075, and 1175 degrees Fahr. (470, 525, 580 and 635 degrees Cent.) using dry ammonia gas and ammonia gas which had been bubbled through aqueous solution of ammonia. The results obtained seemed to show little difference in either the depth or hardness of the case produced. There was no

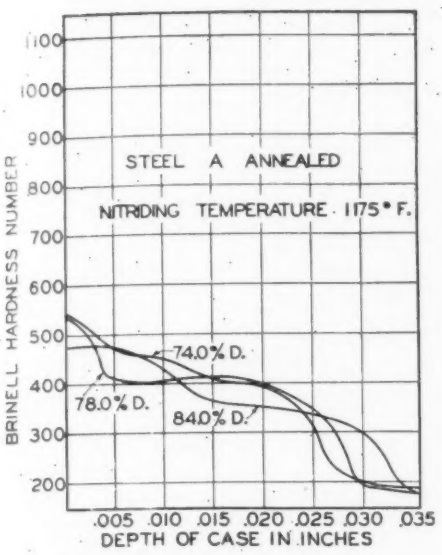


Fig. 21—Effect of Dissociation on Hardness of Case. Chromium-aluminum Steel 152A, Annealed. Nitrided at 1175 Degrees Fahr. (635 Degrees Cent.).

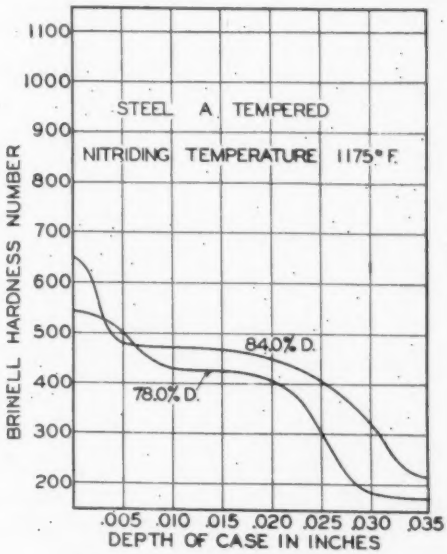


Fig. 22—Effect of Dissociation on Hardness of Case. Chromium-aluminum Steel 152A, Tempered. Nitrided at 1175 Degrees Fahr. (635 Degrees Cent.).

consistent relation between the color obtained on the nitrided surface and the moisture content of the ammonia gas.

Effect of Gas Decomposition on Hardness and Depth of Case.—By means of controlling the rate of gas flow through the nitriding chamber it has been possible to produce different percentages of dissociation at each of the different nitriding temperatures. Tests have been made on chromium-aluminum steel 152A in both the annealed and tempered condition for the four temperatures discussed in this investigation. Some of the tests have been made on chromium-vanadium steel in the tempered condition. The results of tests on steel 152A and the chromium-vanadium steel are shown in Figs. 15 to 24 inclusive.

From a study of these graphs certain generalizations may be drawn, although the results are not entirely consistent. For the chromium-aluminum steel 152A in the annealed condition, it seems that the surface hardness increases with increase in dissociation. On the other hand, in the majority of tests slightly greater penetration was obtained with lower dissociation. For the tempered specimens this condition seems to have been reversed. For chromium-vanadium steel which was tested only in the tempered condition, the lower dissociation seemed to give a higher surface hardness and the greater dissociation a greater depth of penetration, which is more

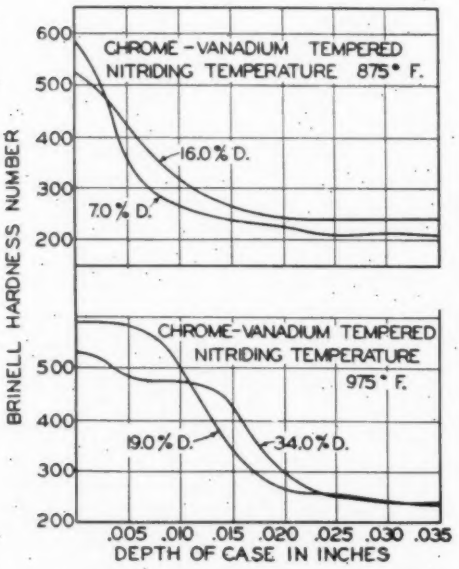


Fig. 23—Relation of Dissociation to Case Hardness of Chromium-vanadium Steel, Tempered. Nitrided at 875 and 975 Degrees Fahr. (470 and 525 Degrees Cent.).

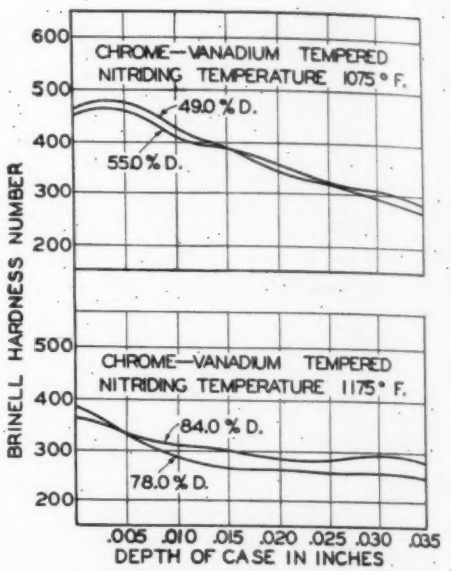


Fig. 24—Relation of Dissociation to Case Hardness of Chromium-vanadium Steel, Tempered. Nitrided at 1075 and 1175 Degrees Fahr. (580 and 635 Degrees Cent.).

nearly in agreement with the results obtained with steel 152A in the tempered condition. Nitriding temperature seemed to control the surface hardness and depth of penetration and is a more important factor than the percentage of dissociation in all cases.

Relation of Nitriding Temperature to Hardness and Depth of Case.—The results of tests on the chromium-aluminum steel 152A at four different temperatures and at three different rates of gas flow are shown in Figs. 25, 26 and 27. In Fig. 25 the chromium-aluminum steel 152A is in the annealed condition while in Figs. 26 and 27 the results represent both the annealed and the tempered specimens.

The general relation, that nitriding temperature increases with depth of case increases, is well established. For the annealed specimens nitriding temperature of 975 degrees Fahr (525 degrees Cent.) gave a higher surface hardness than 875 degrees Fahr. (470 degrees Cent.) but the values decrease rapidly at 1075 and 1175 degrees Fahr. (580 and 635 degrees Cent.). For the tempered specimens the maximum surface hardness was obtained at 875 degrees Fahr. and then decreased for all the higher nitriding temperatures studied.

The results of tests on the chromium-vanadium and chromium-nickel-molybdenum steels in the tempered condition for four different nitriding temperatures and two rates of flow of gas are shown in

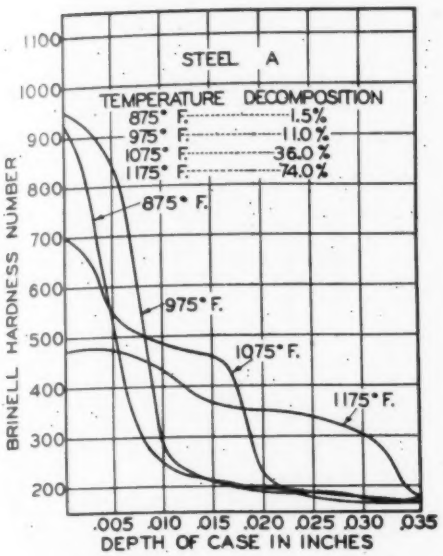


Fig. 25—Effect of Nitriding Temperature on Case Hardness. Chromium-aluminum Steel 152A.

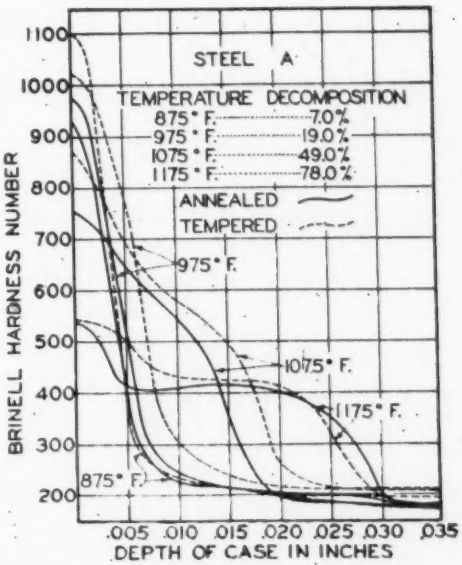


Fig. 26—Effect of Nitriding Temperature on Case Hardness. Chromium-aluminum Steel 152A, Annealed and Tempered.

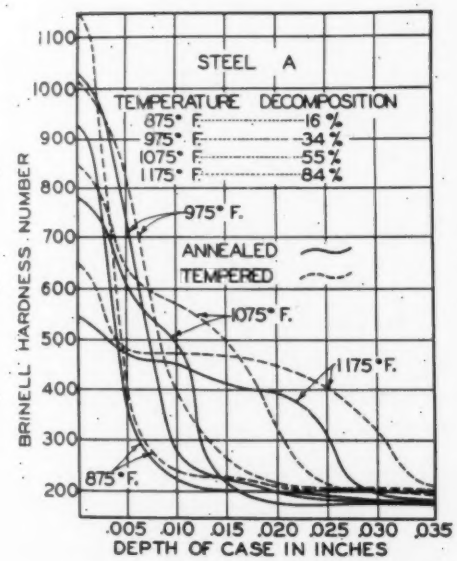


Fig. 27—Effect of Nitriding Temperature on Case Hardness. Chromium-aluminum Steel 152A, Annealed and Tempered.

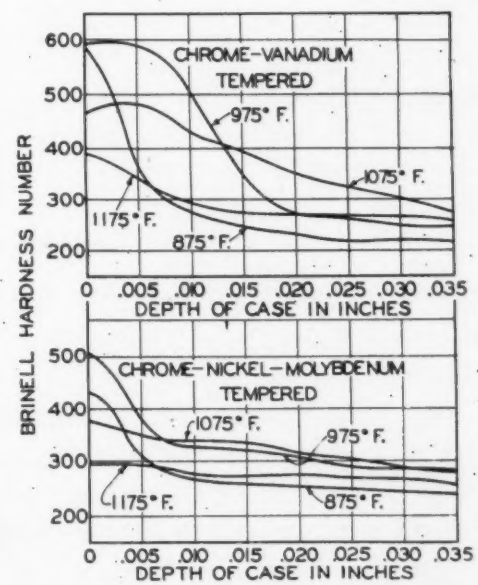


Fig. 28—Effect of Nitriding Temperature on Case Hardness of Tempered Chromium-vanadium and Chromium-nickel-molybdenum Steels.

Figs. 28 and 29. The maximum surface hardness for the chromium-vanadium steel was obtained by nitriding temperature of 975 degrees Fahr. At 975 degrees Fahr. the steel showed a considerably greater depth of penetration than 875 degrees Fahr. At 1075 degrees Fahr.

the steel also shows greater depth of penetration with considerable falling off in the hardness for depths up to 0.010 to 0.015 inch. The hardening effect at 1175 degrees Fahr. (635 degrees Cent.) was rather unimportant. The hardness of this chromium-vanadium steel as compared with the chromium-aluminum steel 152A when determined by the Vickers instrument is considerably less than might

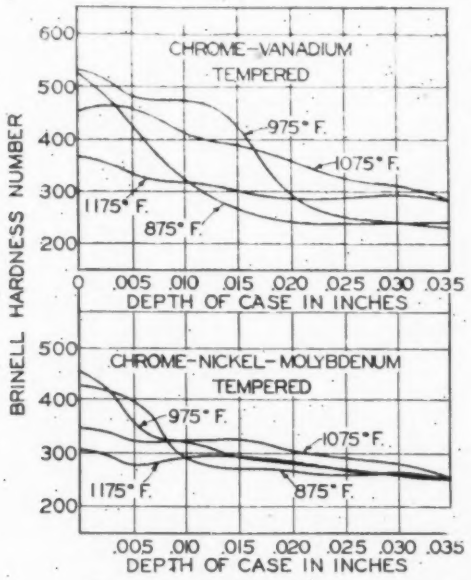


Fig. 29—Effect of Nitriding Temperature on Case Hardness of Tempered Chromium-vanadium and Chromium-nickel-molybdenum Steels.

have been anticipated from the results of scleroscope tests in Part I of this investigation. This steel was found to respond to the nitriding treatment sufficiently for certain types of service but is not sufficiently hard for a number of types of service, so it is impossible to predict its importance in nitriding. In the case of chromium-nickel-molybdenum steel the hardness values are still lower but the same general relations with reference to surface hardness, depth of penetration as a function of the nitriding temperature have been found to obtain.

Loss of Carbon During Nitriding.—Our first tests to determine the loss of carbon during nitriding were made on chromium-aluminum steel 152A which was in the form of fine turnings. The sample was nitrided at 875 degrees Fahr. (470 degrees Cent.) for 23 hours, and carbon determinations showed no loss in carbon. In later tests, in which three steels were used and nitriding temperatures of

875, 975, and 1075 degrees Fahr., we found consistent loss in carbon content during nitriding. The loss was slight at 875 degrees Fahr. and increased as the temperatures increased, as shown in Table VIII.

The above tests were made over a period of 50 hours. Table IX shows in addition the per cent decomposition of the ammonia

Table VIII
Composition of Steels Used to Determine Loss of Carbon During Nitriding

Steel No.	C	Mn	P	S	Cr	V	Al	Mo	Si
79	.361	0.58	.014	.042	....	....	....	....	....
152A	.371	0.50	.014	.020	1.61	....	0.84	....	0.34
94A	.348	0.70	.013	.029	.84	0.19	....	....	0.18

Table IX
Loss of Carbon During Nitriding at Different Temperatures

Steel No.	% C Before Nitriding	% C After Nitriding at 875°F.	975°F.	1075°F.
79	0.361	0.329	0.310	0.212
152A	0.371	0.354	0.321	0.271
94A	0.348	0.323	0.314	0.235
Ave. Decomposition		13%	43%	56%

gas. These experiments tend to show that there is a fairly good relation between the amount of gas decomposition and the loss of carbon during nitriding. There is a noticeable decrease in the amount of carbide during nitriding as shown by the changes in the microstructure, and this is in agreement with the loss as determined by chemical analysis.

Conclusions

One of the significant results of this investigation is the limitation of certain methods of testing applied to extremely hard cases. Apparently the true hardness of the case is not shown by the scleroscope when the Brinell hardness exceeds about 600.

The curves included in this report show that the relations of such factors as rate of gas flow, amount of decomposition of the gas, nitriding temperature, and condition of steel, to the character of the case produced.

The detail of the mechanism of the hardening of steel by nitriding appears to require further study.

Acknowledgments

The writers are indebted to C. H. Green for assistance in the preparation of the manuscript and to C. H. Green and J. C. Sanderson for assistance in photographic work.

DISCUSSION

Written Discussion: By Robert Sergeson, Central Alloy Steel Corp., Canton, Ohio.

The authors have contributed a very interesting and instructive paper and should be congratulated for their efforts.

In discussing this paper I have picked out the subjects which we also have investigated. The first is:

Porous Condition. The porous condition found on the surface of nitrided specimens has been an unusual occurrence to the writer. Two causes

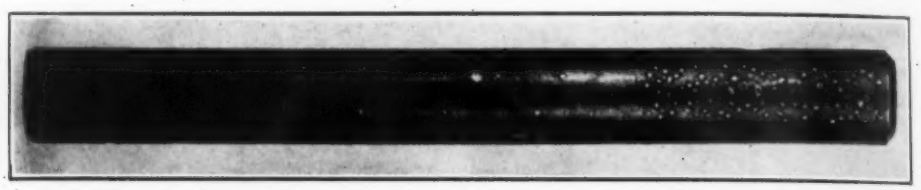


Fig. 1—Showing Blisters on Nitrided Pump Shaft Due to Air Leakage. ⅔ size.

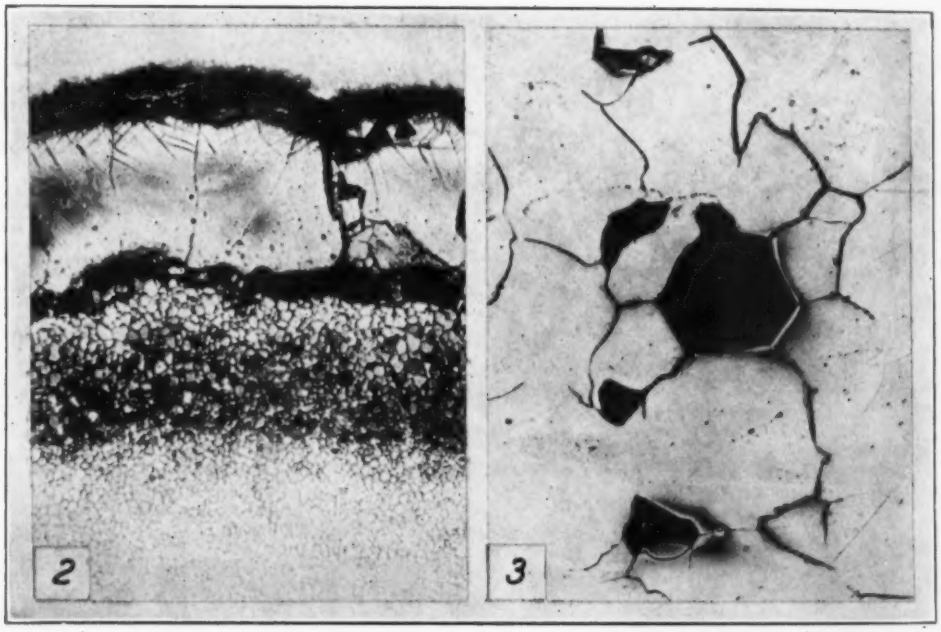


Fig. 2—Showing Decarburized and Nitrided Area Spalling from Surface. × 100.
Fig. 3—Nitrided Decarburized Area after Polishing and Etching. Note Entire Grain Fallen Out, also Lack of Cohesion. Nital Picric Etch. × 100.

have been attributed to it. The first is to have an air leak in the nitriding pot which has been known to cause this condition and even to raise blisters on the steel. Fig. 1 shows a pump shaft illustrating this condition. The second cause is the nitriding of a decarburized surface in which the case is brittle and readily spalls. Fig. 2 shows such a case. Fig. 3 shows a grain in the nitrided decarburized area to have actually

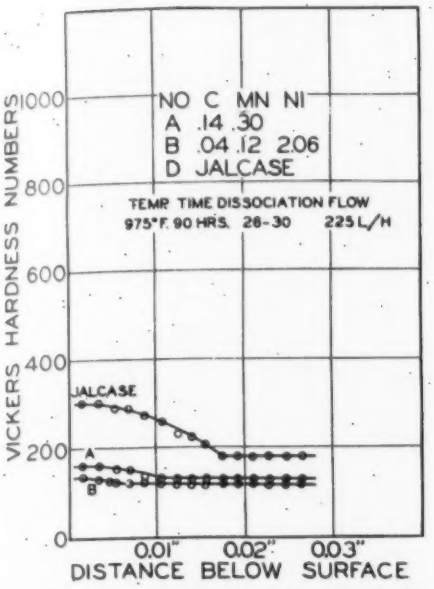


Fig. 4—Nitriding of Carbon Carburizing Steels.

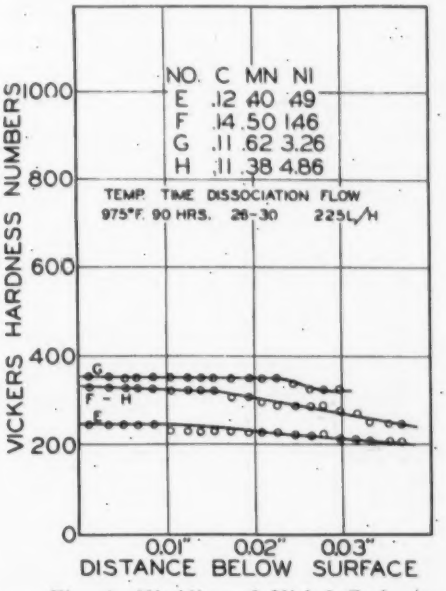


Fig. 5—Nitriding of Nickel Carburizing Steels.

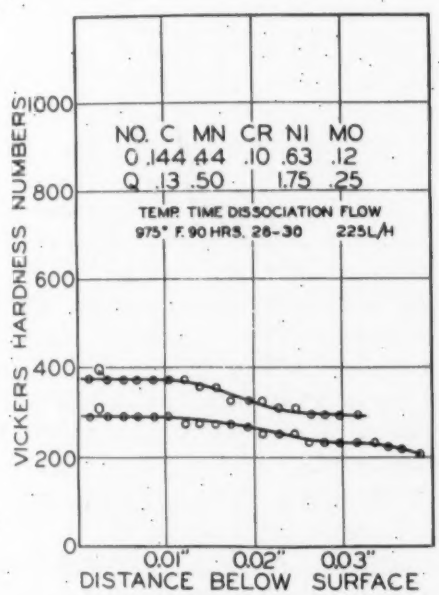


Fig. 6—Nitriding of Nickel-Molybdenum Carburizing Steels.

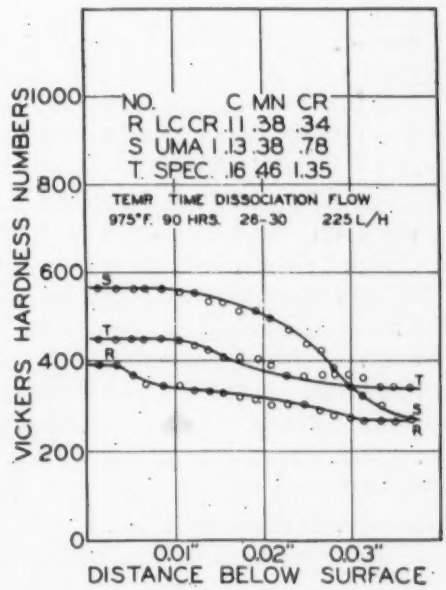


Fig. 7—Nitriding of Chromium Carburizing Steels.

fallen out in the grinding and polishing, illustrating the lack of cohesion between grains.

Carbide Size. The carbide size in nitriding has no effect upon the surface hardness and but little upon the penetration. Such are the results of nitriding for 90 hours, specimens of aluminum-chromium steel of the same analysis in the heat treated, normalized and annealed state. Like

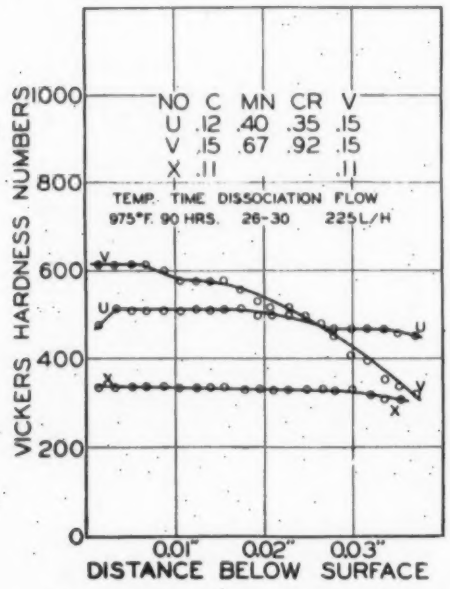


Fig. 8—Nitriding of Chromium-Vanadium Carburizing Steels.

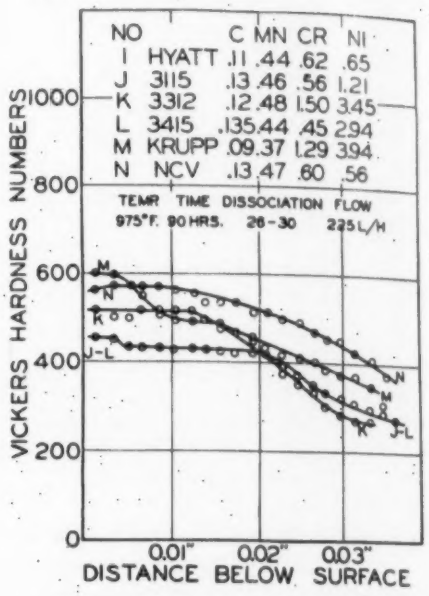


Fig. 9—Nitriding of Chromium-Nickel Carburizing Steels.

surface hardness was obtained on all while the heat treated specimens gave only a slightly better penetration. However, carbide size is quite important from the standpoint of toughness. The highest toughness of the nitrided case is obtained on the heat treated specimens (quenched and tempered).

Nitriding of S. A. E. Analyses Steels. I am in agreement with the authors' work on the nitriding of the many S.A.E. steel analyses. The charts shown in Figs. 4, 5, 6, 7, 8 and 9 show the results of a 90-hour nitriding cycle at 975 degrees Fahr. on "as rolled" specimens of carburizing types. The actual analyses are shown on the charts. Thus the carbon, nickel, and nickel-molybdenum steels show only slight ability to nitride whereas the chromium, chromium-vanadium and chromium-nickel steels show quite a marked ability to nitride. However, in no case does the hardness even approach that obtained by the Krupp analyses.

Written Discussion: J. P. Walsted, Massachusetts Institute of Technology, Cambridge, Mass.

The authors call attention to the apparent decrease in the amount of carbide during the nitriding operation. Dr. Homerberg and I have noticed this on numerous occasions. At first, this was thought to be due to decarburization during the process. Investigation has shown that the introduction of nitrogen into steel changes the iron to the gamma condition in which the carbides are soluble. The disappearance of the carbides is due mainly to their being taken into solution.

The authors state that carbides are necessary to the nitriding operation. This is an interesting theory which will bear some further investigation. Dr. Homerberg and I have found that low carbon materials,

such as the now obsolete nitriding steel C, tends to form more of the network structure than higher carbon materials, though satisfactory case depth is readily obtained.

The authors call attention to the superior properties of the nitrided case when a previously heat treated specimen is used. This is a detail that cannot be too strongly emphasized. I should like to add that previously heat treated steel showed less tendency to form the network structure and was, therefore, less liable to brittleness.

The general impression has been that dry ammonia is necessary in nitriding. I agree entirely with the authors that water vapor in moderate amounts has little influence on the nitriding operation. At high magnifications, a slightly greater tendency to form network is shown when using ammonia containing water vapor. This, however, can be detected only at higher magnifications.

I wish to congratulate the authors on their thorough study of the influence of composition of the steel. This detail is of the greatest importance and is often overlooked or neglected.

Oral Discussion

A. B. KINZEL: I should like to go a little further with the thesis discussed by Mr. Eaton. He said that in order to rate steels for nitriding, we must have a great many tests. This is undoubtedly true. However, to determine which steels should be used for making these tests we must have a preliminary knowledge of a great many steels. It seems to me that Dr. Harder and his co-authors have done a real service from this point of view. I do not agree with all of their conclusions; in fact, actual study of their tables leads to possible conclusions at variance with those drawn. However, the point is that they have presented data from which we can proceed. I am disappointed in the choice of some of the steels. For example, 3 or 4 vanadium steels restricted in each case to maximum of about 0.2 per cent vanadium have been used. The work of other investigators on that subject, including my own paper before this society, 2½ years ago, showed the greater advantage of using a minimum of 0.4 per cent vanadium. A very different order of results would have been obtained, I am sure.

I should like to comment on Dr. Harder's use of the Rockwell ball. In our work at the Union Carbide and Carbon Research Laboratories we use it for a quick rough and ready test. It gives the integrated effect of case depth and case hardness. It appears to me to be a test that might well be applied in the plant, because of its speed and the information obtained. I might also add that in the matter of testing for ductility the use of the Brinell ball has been found to give very consistent and valuable information, by observing the type of cracking in the impression.

Authors' Closure

In reply to Mr. Sergeson's discussion it must be admitted that Mr. Sergeson has made quite a good case for his contention that a decarburized

surface produces a porous rim. It would be difficult for us to establish definitely that the steels used in our tests and shown in Figs. 8 and 9 were not in any way decarburized. Such a condition seems rather improbable because the surface was always removed before nitriding and there was practically no chance for air to get into the nitriding chamber.

I wish to raise the question of the possibility of certain steels forming a microconstituent during the nitriding process which has a much larger volume than the normal constituent and which may produce porosity even in steels which are not decarburized. We have not found this porosity to any extent in such alloys as Steel A, which is more nearly the type which Mr. Sergeson has given most attention.

With regard to the effect of carbide particle size, there are apparently two or three reasons why the steels should be heat treated, that is, quenched and tempered, before nitriding. The first one which we were considering is the improved properties of the core. It so happened that we made our first tests and our first experiments on a chrome-molybdenum steel and there was a noticeable increase in the hardness of those samples which showed fine particle size. We found this relation to hold true in general; for example, this is shown in Figs. 15 and 16, using the Steel A at a temperature of 875 degrees Fahr. At 975 the difference is less pronounced. There would seem to be sufficient reason for heat treating the parts before nitriding for the purpose of improving the properties of the core.

In reply to Dr. Walsted's discussion, I am pleased to note that our results are in such good agreement. There is one point which Dr. Walsted has mentioned which requires some reply. Our statement probably should have been modified somewhat so as to say that carbides are apparently necessary for satisfactory nitriding. The cases which we obtained by nitriding materials free from carbides, or even very low in carbides, were decidedly unsatisfactory.

In reply to Mr. Kinzel's discussion the following comments will apply. We realized at the time that we were not including a complete study of all the possible compositions of the steels. The element of time required for such an investigation is evident. We used steels which were readily available, knowing at the time that additional and, very likely, valuable results would be obtained by including many other compositions. It was not our intention to say that the Vickers instrument was the only one which would give valuable results. It has been our experience, however, that we were able to show greater differences in hardness and to identify the extremely hard cases better by means of the Vickers instrument than by the others which we had tried.

INVESTIGATIONS IN NITRIDING

By Robert Sergeson

Abstract

This paper is divided into three sections. The first discusses the reasons for the change from the former to the present nitriding analysis. Also nitrided and carburized cases are compared in respect to hardness penetration and the effect of reheating temperatures on the hardness of the case. The second section offers new data in regard to (1) the effect of increased flow of ammonia gas, (2) the effect of increase in nitriding temperature in lowering hardness of case, (3) the effect of varying aluminum content, (4) the effect of nickel, and (5) the duplex methods of nitriding. In the third section, decarburization and brittleness are discussed. A method for removing brittleness is shown.

Section I

THE outcome of Fry's[1] work on nitriding steels was a series of chromium-aluminum steels of varying carbon content. These were experimented with successfully on the continent of Europe. Later the chromium-nickel-aluminum series was tried and discarded due to the temper brittleness of the core, resulting from the long heating periods of the nitriding cycle within the temper brittle range of this type. Later still molybdenum was added to the chromium-aluminum steels and found to add toughness. The first steels to be experimented with in this country were the chromium-aluminum and the chromium-aluminum-molybdenum. The former rapidly gave way to the latter.

In general the early analysis was—

chromium 1.30 to 1.80 aluminum 1.30 to 1.80 molybdenum 0.20 to 0.30

Investigations, some of which are included in this report, will show the reasons for the change to the present analysis range used for nitriding.

[1]Dr. Adolph Fry, "Nitrogen in Iron, Steel and Special Steels"—*Kruppsche Monatshefte*, September, 1923.

The author, a member of the society, is associated with the research laboratories of the Central Alloy Steel Corp., Canton, Ohio. Manuscript received July 10, 1929.

The present range is chromium 0.80 to 1.30, aluminum 0.60 to 1.20, molybdenum 0.15 to 0.25. The facts that this latter analysis gave excellent surface hardness and penetration with better adaptability to making, forging and machining were the reasons for its selection.

For the early history of nitriding leading up to Fry's work, the reader is referred to the papers of Leon Guillet.[2]

Nitriding Versus Carburizing

For the first time carburizing is giving way to a newer method of surface hardening. Many places are being found where the nitrided steels are replacing the carburized parts. In view of this inevitable competition a comparison of the hardness penetration would well illustrate the cause. Two typical carburizing steels were selected for the present study. These were nickel-molybdenum (S.A.E. 4615), an oil quenching type, and chromium-vanadium (S.A.E. 6115), a water quenching type. Both of the latter steels were carburized for eight hours at 1690 degrees Fahr. (920 degrees Cent.), double-quenched and tempered at 300 degrees Fahr. (150 degrees Cent.); these being accepted treatments given in the A. S. S. T. 1929 Handbook. For comparison with these a chromium-aluminum-molybdenum steel of 0.34 per cent carbon was used. This specimen received the following treatment: heat treated at 1650 degrees Fahr. (900 degrees Cent.), oil-quenched and tempered at 1250 degrees Fahr. (675 degrees Cent.), machined, ground and nitrided for 90 hours at 975 degrees Fahr. (525 degrees Cent.).

The specimens were approximately ½ inch square by 1 inch long. They were ground on a 3-degree taper after being hardened and the Vickers hardness readings using a 10-kilogram load taken on the tapered surface. The first ten readings, starting at the surface, were taken 1/60 of an inch apart and the remaining readings 1/20 of an inch apart. This method was employed in the taking of all hardness gradation readings and is the same as employed by Eaton.[3]

The results of this work are shown by the curves in Figs. 1

[2]Leon Guillet, "The Nitriding of Steel and Its Industrial Application", *Le Genie Civil*, July 9, 16 and 23, 1927.

[3]G. M. Eaton, "Methods of Approximating Certain Physical Characteristics of Nitrided Steel Cases", Transactions, American Society for Steel Treating, Vol. XV, January, 1929, pp. 1-35.

and 2, in which the Vickers hardness values are plotted against the graduating distances below the surface. A study of these curves shows—

1. That the nitrided case is clearly far superior as regards hardness

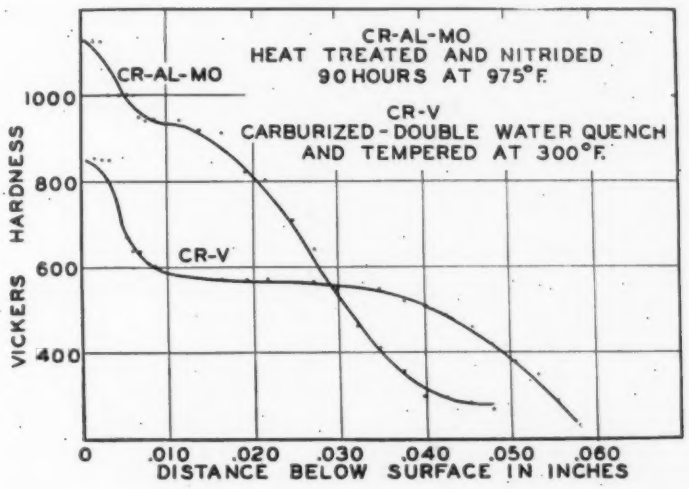


Fig. 1—Relation of Hardness Penetration of Chromium-aluminum-molybdenum and Carburized Chromium-vanadium Steels.

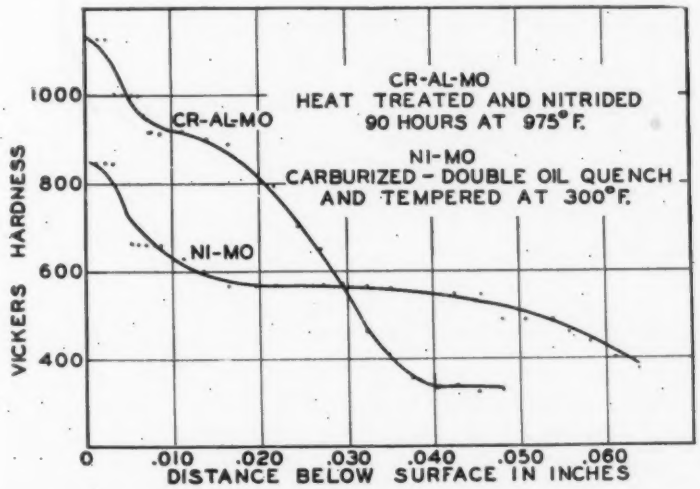


Fig. 2—Relation of Hardness Penetration of Chromium-aluminum-molybdenum and Carburized Nickel-molybdenum Steels.

up to a case depth of 0.030 inch and below this depth the carburized specimens are the harder. That this higher hardness of the nitrided case means greater resistance to wear has already been proved by service tests on cam shafts and wrist pins, etc.

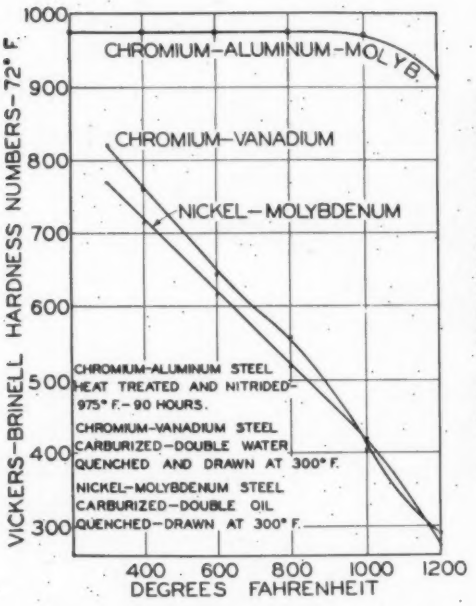


Fig. 3—Effect of Reheating Temperatures on Hardness of Surface of Nitrided and Carburized Steels.

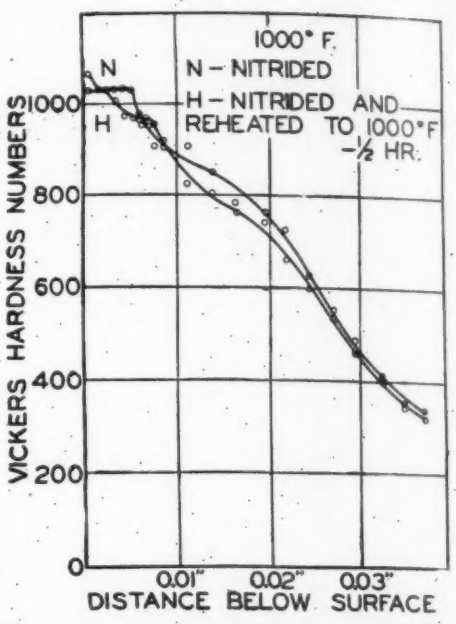


Fig. 4—Effect of Heating to 1000 degrees Fahr. on Hardness of Case Gradation.

2. The gradation of hardness of the nitrided case to its core is gradual, there being no sharp break in the curve. This is also true of the carburized types and is indicative of a strong union between case and core, which is essential to prevent chipping or spalling of the case.
3. It is further noted that the type of hardness gradation curve is the same for both the oil and the water hardened carburizing steels.

Effect of Reheating Temperature on Hardness of Case

The effect of reheating specimens treated as above at varying temperatures was investigated. The specimens were reheated to 300 degrees Fahr. (150 degrees Cent.) under iron drillings to prevent scaling of surface and after again cooling to room temperature the Vickers hardness of the surface was taken. The same specimens were again reheated to 500, 700, 900, 1100 and 1200 degrees Fahr. (260, 370, 485, 595 and 650 degrees Cent.) in a like manner and the hardness of the surface obtained after each reheating. The hardness values resulting, plotted in curve form, are shown in Fig. 3. Following the upper curve in this Fig. 3 it is noted that the

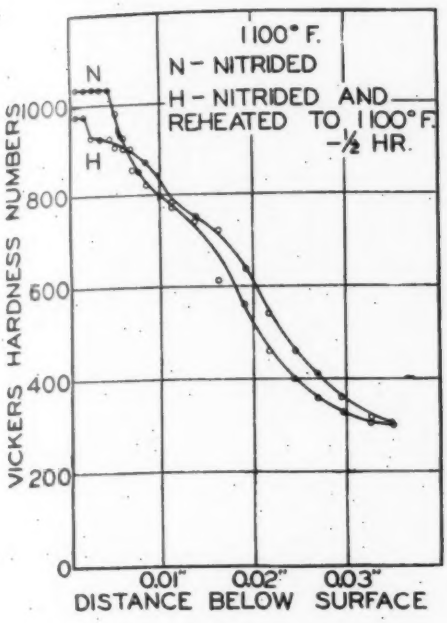


Fig. 5—Effect of Heating at 1100 degrees Fahr. on Hardness of Case Gradation.

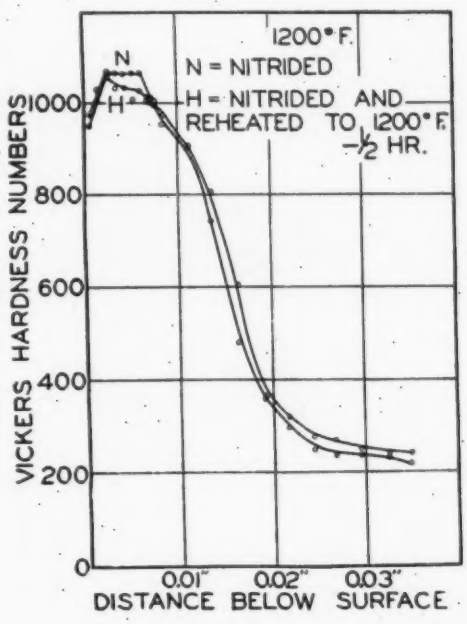


Fig. 6—Effect of Heating at 1200 degrees Fahr. on Hardness of Case Gradation.

case retains its high hardness without any loss up to 1100 degrees Fahr. (595 degrees Cent.) and falls off but slightly with the 1200 degrees Fahr. (650 degrees Cent.) temper. The two carburized cases show an immediate and progressive decrease in hardness with the increase in tempering temperature.

Other nitrided cases were further investigated by obtaining the hardness gradation "as nitrided" and after being reheated at elevated temperatures. Curves shown in Figs. 4, 5 and 6 give the results after heating for one-half hour at 1000, 1100 and 1200 degrees Fahr. (540, 595 and 650 degrees Cent.). From these results it is seen that the hardness of the entire case gradation is unaffected by the reheating temperatures. The fact that the hardness of the case was not materially affected by reheating to 1200 degrees Fahr. (650 degrees Cent.) is quite important and will be referred to again in Section III. The reheating was continued to include 1800 degrees Fahr. (980 degrees Cent.). This latter and all intervening temperatures failed to soften, for specimens reheated to 1800 degrees Fahr. are still file hard and give a hardness of 900 Vickers Brinell. Lead was used as the heating medium for specimens reheated above 1300 degrees Fahr. (705 degrees

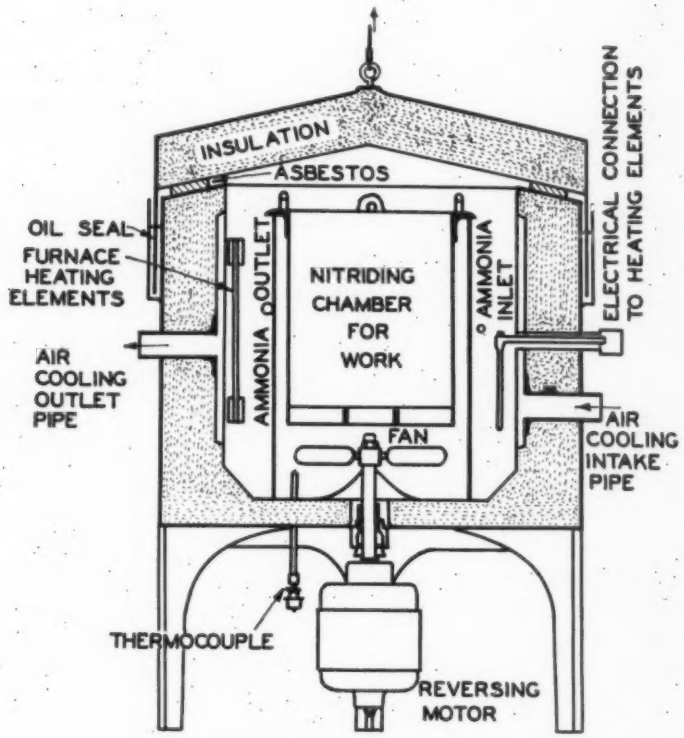


Fig. 7—Sketch showing cross-section of Nitriding Furnace Used.

Cent.), the reason for this being to prevent the scaling away of the surface as the nitrided case scales much in the same manner as ordinary steels do when heated to elevated temperatures. Thus it is apparent that the nitriding steels when hardened by the nitriding process cannot be softened for re-machining by the simple means of reheating.

Section II

Experiments in Nitriding

Having found that erratic results were obtained when nitriding in small tubes, the following experiments were, therefore, carried out in what may be termed a small production nitriding unit. The brief description following will give some idea as to the size and method of operation of this unit. Fig. 7 shows a cross-section of the nitriding furnace used. The size of the nitriding chamber is 14 inches in diameter and 16 inches deep. The heating elements of the furnace are exposed to the gases of the nitriding process. A fan is located in the bottom of the furnace. This fan revolves

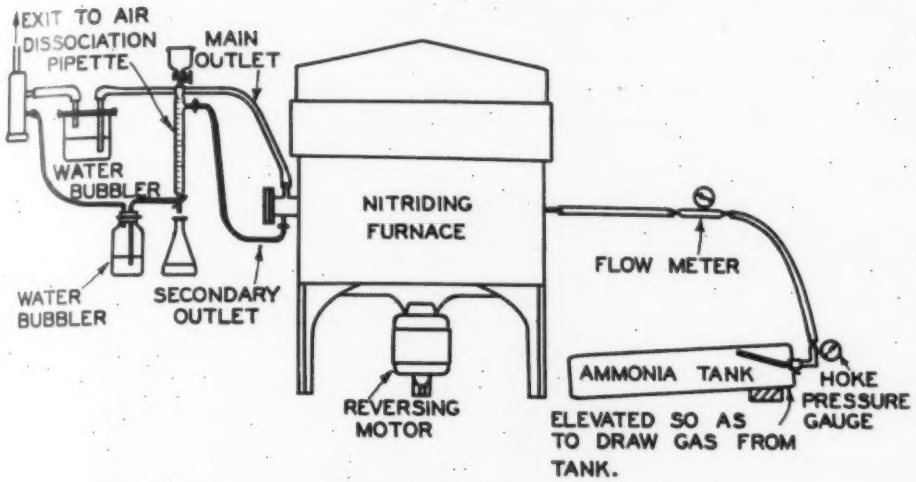


Fig. 8—Schematic Sketch showing Set-Up of Nitriding Equipment.

at 1750 revolutions per minute and reverses every minute, thus insuring uniform circulation and temperature. Fig. 8 shows a schematic arrangement for the nitriding operations. At the lower right hand corner of the sketch is an ammonia tank which is so arranged as to draw ammonia gas and not liquid. A needle valve on the ammonia tank controls the flow of gas which passes through a flow meter which records the rate of flow of the gas passing into the nitriding furnace. The gases upon leaving the nitriding furnace have two paths, one directly to the exit, the other to a dissociation pipette and thence to the exit. With this method, a dissociation may be obtained quickly at any time during the run. Fig. 9 shows a photograph of the dissociation pipette.

Due to the temperature of nitriding and the catalytic effect of the material being nitrided, the ammonia gas is partially broken up into constituents hydrogen and nitrogen. Thus the exit gases from the nitriding furnace consist of ammonia (NH_3), hydrogen (H_2) and nitrogen (N_2). Of these three gases, only the ammonia is soluble in water. Therefore if these gases are passed through the dissociation pipette, entering through the middle stopcock and leaving through the lower three-way stopcock, a 100 cubic centimeters of the gases (capacity of the pipette) may be trapped at any time by closing simultaneously the latter two stopcocks. The upper stopcock is closed during the above procedure and the reservoir above the upper stopcock filled with water. After the gases are trapped in the pipette, the upper stopcock is opened and water will flow into the pipette as long as any ammonia gas remains. For example, if

the water rises to 70 cubic centimeters it is evident that 70 cubic centimeters of the exit gases were ammonia and the remaining 30 centimeters are the insoluble hydrogen and nitrogen. The percentage dissociation referred to in this paper is the percentage of

Fig. 9—Dissociation Pipette.

insoluble gases, hydrogen and nitrogen, in the exit gases, which in the above case would be 30 per cent. While this is not strictly the true dissociation, it gives a satisfactory basis for comparison.

Effect of Temperature and Flow in Nitriding

To study the effect of temperature and flow in nitriding, sixteen analyses were investigated. However, as all of these show the same trend, only four of them, analyses to be found in Table I, will be discussed. In all cases the specimens were heat treated at 1650 degrees Fahr. (900 degrees Cent.), oil-quenched and tempered at 1200 degrees Fahr. (650 degrees Cent.), machined and ground before being nitrided. The size of the finished specimens was ½ inch square by 1 inch, which after being nitrided was taper-

ground and tested for hardness gradation as previously explained. The first of investigations was to keep the flow of ammonia constant at 50 liters per hour, the time element constant at 48 hours and vary the temperature as follows—950, 1000, 1100 and 1200

Table I
Typical Analyses of Steels Used to Study Effect of Temperature and Flow in Nitriding

No.	C	Mn	Si	Cr	Mo	Al	V
3305	0.315	0.63	0.15	1.68	0.19	0.70	...
6124	0.28	0.58	0.09	1.68	...	0.73	0.07
381	0.50	0.50	0.24	1.68	0.26	0.58	...
408	0.35	0.66	1.00	0.98	0.23	0.58	...

degrees Fahr. (510, 540, 595 and 650 degrees Cent.). The results of this set suggested a second set in which the time and temperatures remained the same as in the first set but the flow increased

Table II
Decarburization Tests on a Chromium-Aluminum-Molybdenum Nitriding Steel Drillings

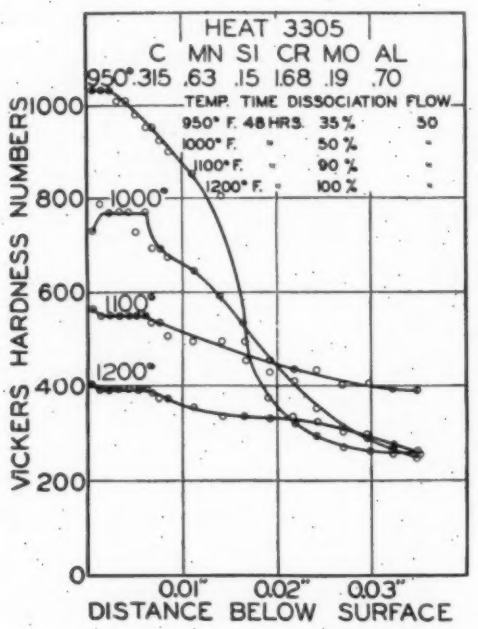
	Carbon Content
Before nitriding	0.335
After nitriding at 950 degrees Fahr., 40 hours	0.13
After nitriding at 1000 degrees Fahr., 40 hours	0.11
After nitriding at 1100 degrees Fahr., 40 hours	0.05
After nitriding at 1200 degrees Fahr., 40 hours	0.02

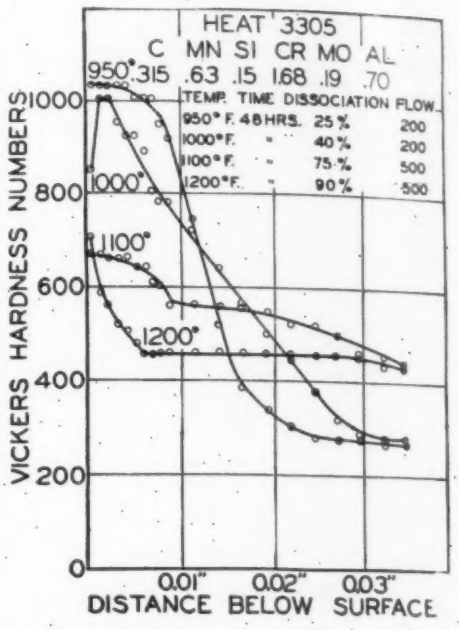
to 200 liters per hour in the 950 and 1000 degrees Fahr. (510 and 540 degrees Cent.) runs and to 500 liters per hour in the 1100 and 1200 degrees Fahr. (595 and 650 degrees Cent.) runs. This was followed and the results are plotted in the curves shown in Figs. 10 to 17, inclusive. A study of these curves points out the following:

1. The increased rate of flow has for temperatures above 950 degrees Fahr. (510 degrees Cent.) given a definite and decided increase in surface hardness and depth of penetration. At 950 degrees Fahr., however, there is little difference in hardness and penetration, due to the increased rate of flow.

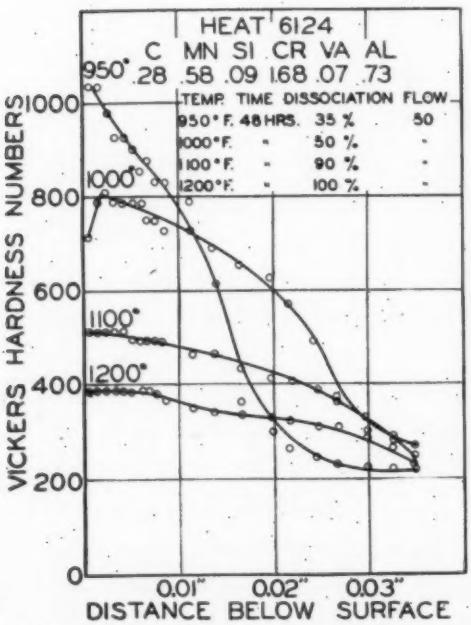
2. As the nitriding temperature increases, the hardness decreases and the penetration increases. Thus 950 degrees Fahr. (510 degrees Cent.) gives the highest hardness and least penetration with 1200 degrees Fahr. (650 degrees Cent.) giving the lowest hardness and greatest penetration.

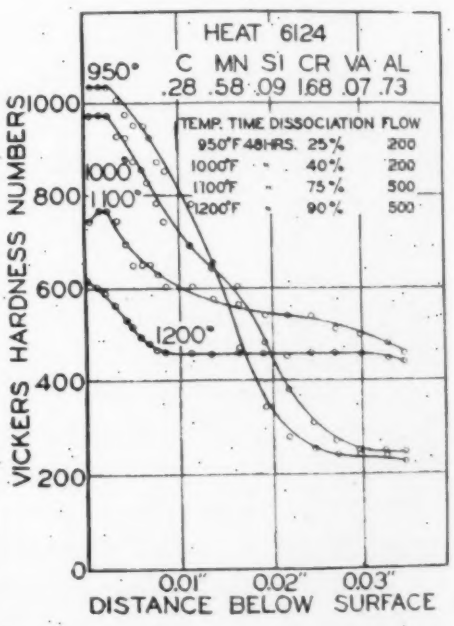
3. That the chromium content may be under 1.00 per cent





Figs. 10 and 11—Effect of Temperature and Rate of Flow on Hardness and Penetration (Heat 3305).

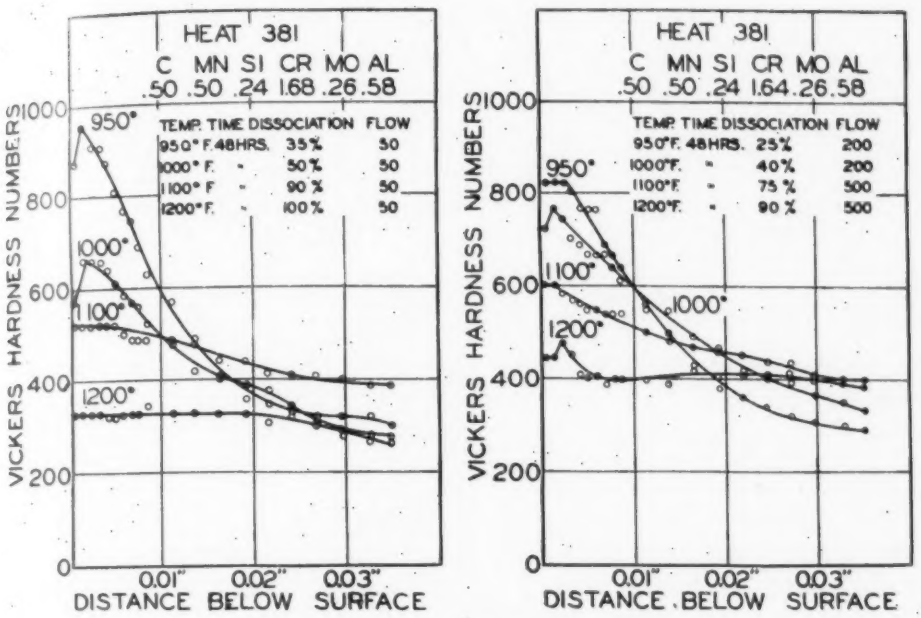




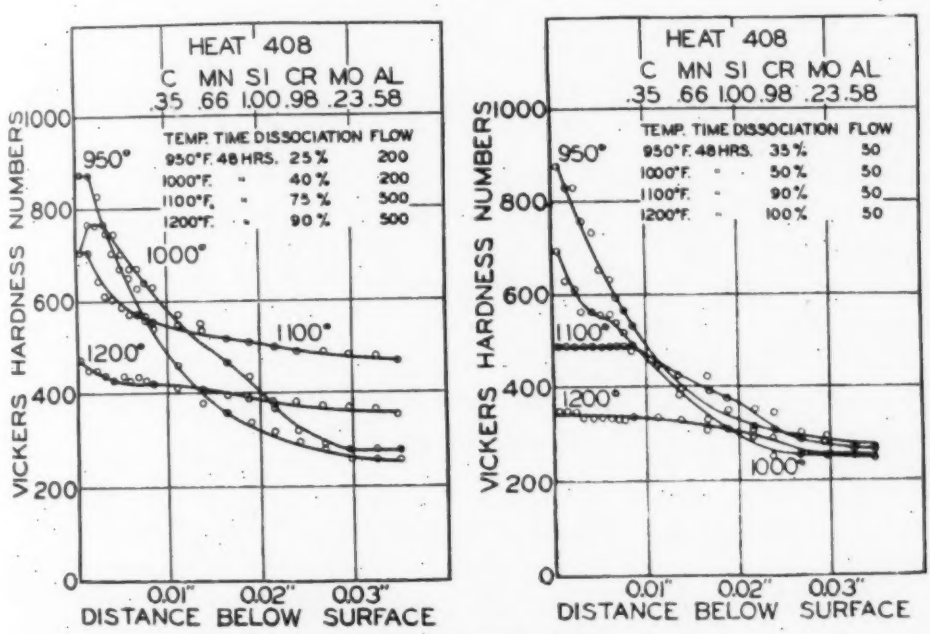
Figs. 12 and 13—Effect of Temperature and Rate of Flow on Hardness and Penetration (Heat 6124).

is indicated by the results of heat 408 when comparing with heat 381.

4. That lower aluminum contents may be used is also in-



Figs. 14 and 15—Effect of Temperature and Rate of Flow on Hardness and Penetration (Heat 381).



Figs. 16 and 17—Effect of Temperature and Rate of Flow on Hardness and Penetration (Heat 408).

dicated. This, however, has been proven in later work contained in this report.

5. The increase in rate of flow at a given nitriding temperature decreases the dissociation of the ammonia. This is probably due to mass action or speed of reaction and is to be expected.

Each of the specimens in the above cycles was polished on the taper-ground surface and the case examined. The polished surface was etched with a nital picric solution.[4] At the extreme surface of all specimens after etching there is observed a white constituent which gives the appearance of ferrite. Fig. 18 shows this constituent. Unfortunately no drillings of chromium-aluminum-molybdenum steel were placed in the furnace with the above runs.

However, to check this condition, fine drillings of this steel were nitrided at various temperatures for 40 hours and then analyzed for their carbon content. In Table II are shown the results which show that surface decarburization is taking place. It is evident, then, that the white areas are ferrite. Again fine drillings nitrided for 90 hours at 975 degrees Fahr. (525 degrees Cent.) show a carbon content of 0.08 per cent and a nitrogen content of 7.45 per cent, which would substantiate the belief that the white constituent is ferrite with a high percentage of nitrogen in solution.

Beyond this extremely thin decarburized area are found structures which vary, depending upon the nitriding temperature. These are shown in Figs. 19 to 22, inclusive. The structures are much the same, except that the white constituent which partly surrounds some grains with the 950 degrees Fahr. (510 degrees Cent.) cycle becomes heavier with rise in temperature until 1200 degrees Fahr. (650 degrees Cent.) is reached, when the white outline entirely disappears. This would indicate that at 1200 degrees Fahr. (650 degrees Cent.) a diffusion takes place and may take place at somewhat lower temperatures. This will be referred to again in Section III. The above structures are dependent upon the temperature, and independent of the rate of flow.

Effect of Varying Aluminum Content

A further series was run in order to determine the effect of the aluminum content. The four analyses to be found in Table III were obtained and nitrided for 90 hours at 975 degrees Fahr. (525 degrees Cent.). (All specimens were heat treated, machined

[4] 4 per cent picric and 4 per cent nitric acid in ethyl alcohol—10 parts of former to 1 part of latter.

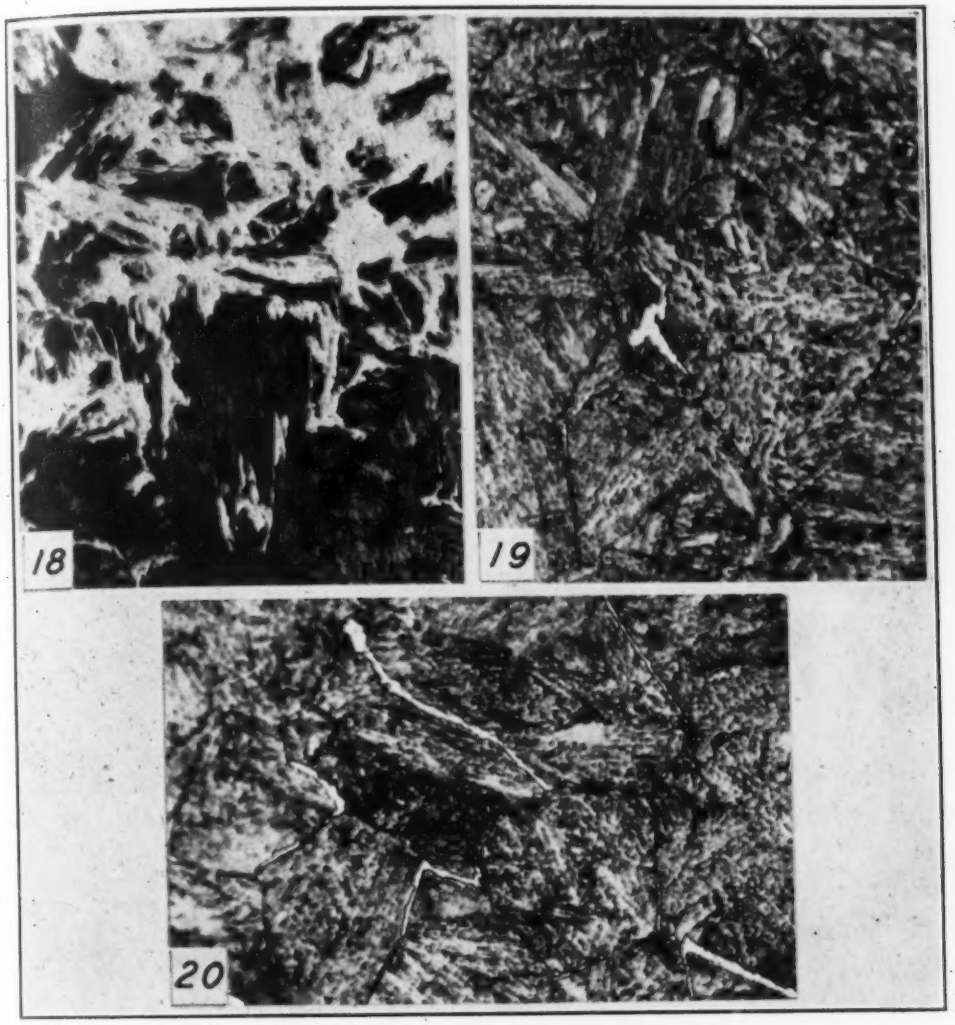


Fig. 18—Showing White Constituent at Surface. × 850.
Fig. 19—Case Nitrided at 950 Degrees Fahr. × 850.
Fig. 20—Case Nitrided at 1000 Degrees Fahr. × 850.

and ground before nitriding.) The specimens were taper-ground and the hardness gradation values plotted, the results of which are shown by the curves in Fig. 23. Here it is brought out clearly that even a small percentage of aluminum in solution with the steel will allow considerable surface hardness and penetration to be obtained. It can be pointed out that the hardness increases with an increase of aluminum content, but that between 0.70 and 1.30 per cent aluminum the rise in hardness is slight. The low first or second reading is due to the decarburization of the surface.

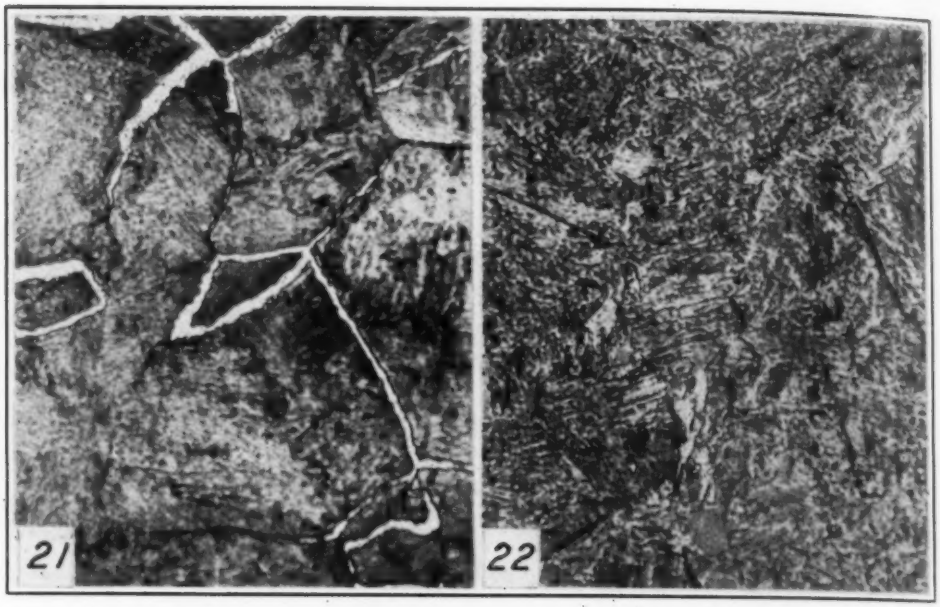


Fig. 21—Case Nitrided at 1100 Degrees Fahr. × 850.
Fig. 22—Case Nitrided at 1200 Degrees Fahr. × 850.

Effect of Nickel

The effect of nickel has been only slightly investigated in this work. Analyses shown in Table IV were nitrided in the same run as the above aluminum series. The results shown in Fig. 24 point to the nickel as retarding the nitriding. Nickel with chromium and aluminum, however, allows excellent surface hardness to be obtained, while nickel with molybdenum and aluminum allow fair hardness but excellent penetration to be obtained. Results suggest that further work should be done with the nickel combinations.

Duplex Runs

Many efforts are being made to reduce the time of nitriding. To accomplish this, the duplex cycles have been suggested. It has been suggested that a high nitriding temperature be employed for a certain time and follow with a low nitriding temperature cycle. However, judging from the results of the reheating of nitrided cases it was thought that the reverse cycle should give the equal or better results. To check this, two cycles were run according to the following conditions:

Cycle A—Nitrided 950 degrees Fahr. (510 degrees Cent.) for

Table III
Analyses of Steels Used in the Study of the Effect of Aluminum Content on Nitriding as Shown in Fig. 23

No.	C	Mn	Si	Cr	Mo	Al
3502	0.32	0.56	0.18	1.43	0.18	1.30
3305	0.32	0.63	0.15	1.68	0.19	0.70
2582	0.34	0.50	0.10	1.62	0.20	0.20
3500	0.32	0.50	0.10	1.57	0.23	0.08

15 hours with 225 liters per hour flow, followed by 1180 degrees Fahr. (640 degrees Cent.) for 15 hours with 500 liters per hour flow.

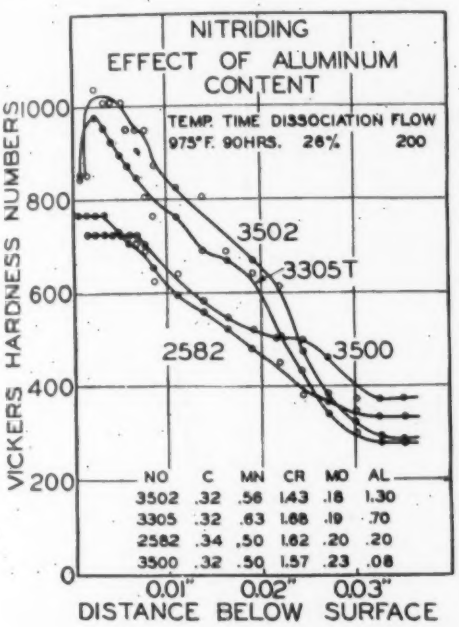


Fig. 23—Effect of Aluminum Content on Hardness and Penetration.

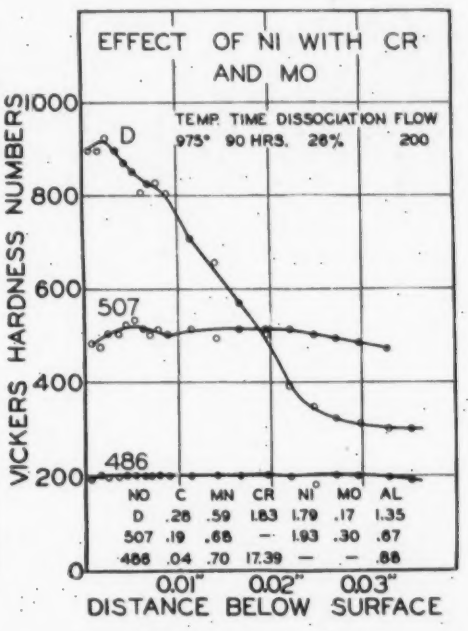


Fig. 24—Effect of Nickel with Chromium and with Molybdenum.

Cycle B—was the reverse of Cycle A, i. e., starting with 1180 degrees Fahr. and ending up with 950 degrees Fahr.

Fig. 25 shows the curves obtained from each cycle and pictures a decided advantage in favor of the Cycle A, which starts with the low temperature first. Further work is to be done regarding these cycles before their commercial adoption can be made. They do, however, show a trend for the reduction of the nitriding time.

Section III

For the preparing and nitriding of the chromium-aluminum-

Table IV
Analyses of Steels Used in the Study of the Effect of Nickel Content on Nitriding as as Shown in Fig. 24

No.	C	Mn	Cr	Ni	Mo	Al
D	0.28	0.59	1.83	1.79	0.17	1.35
507	0.19	0.68	...	1.93	0.30	0.67
486	0.04	0.70	17.39	...	...	0.88

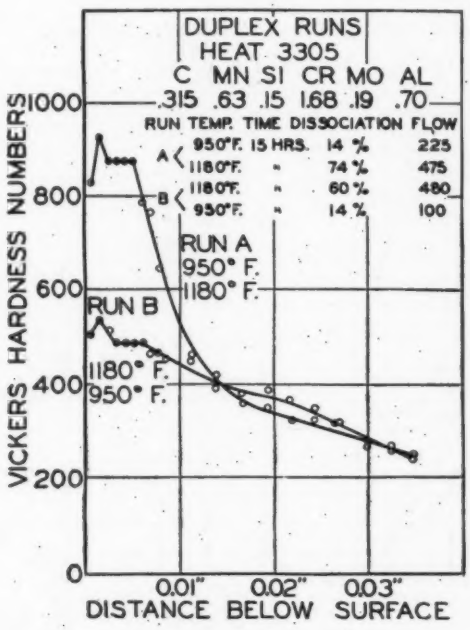


Fig. 25—Duplex Runs.

molybdenum steels, the following data on decarburization and brittleness are offered as being of vital importance.

Decarburization

A great number of the early failures of nitrided products have been traced to this one cause, decarburization. If a decarburized surface is nitrided it becomes very brittle and will readily chip off and in some instances may be crumbled with one's finger nail. Examination of such surfaces under the microscope reveals large nitride needles to be present in the decarburized case. A typical example of this is shown in Fig. 26. In this figure the long nitride needles are easily distinguished in the large decarburized grains. Fig. 27 shows a photomicrograph of the decarburized area at higher magnification. To trace the source of such decarburization and

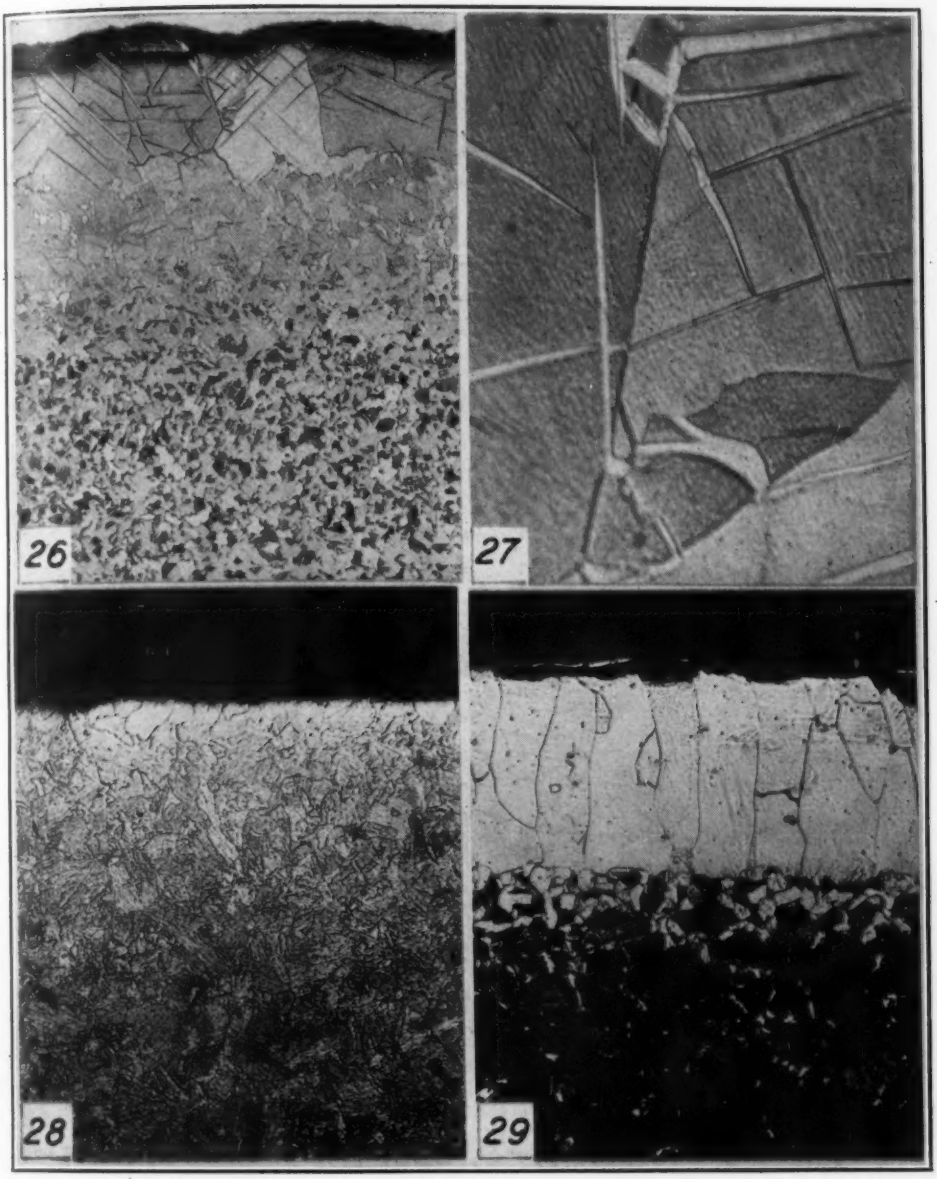


Fig. 26—Nitride Needles in Decarburized Surface. Nital Picric Etch. × 100.
Fig. 27—Showing Needles in Case at Higher Magnification. × 850.
Fig. 28—Surface heated to 1400 Degrees Fahr. for 4 hours. × 100.
Fig. 29—Surface heated at 1600 degrees Fahr. for 4 hours. (1500 Degrees Fahr. shows same condition) Note total decarburization. × 100.

learn the susceptibility of this analysis to decarburization, the following work was undertaken.

For comparison, machined specimens of S.A.E. 4130 steel and chromium-aluminum-molybdenum analysis were reheated at the following elevated temperatures, 1400 to 1800 degrees Fahr. (760 to

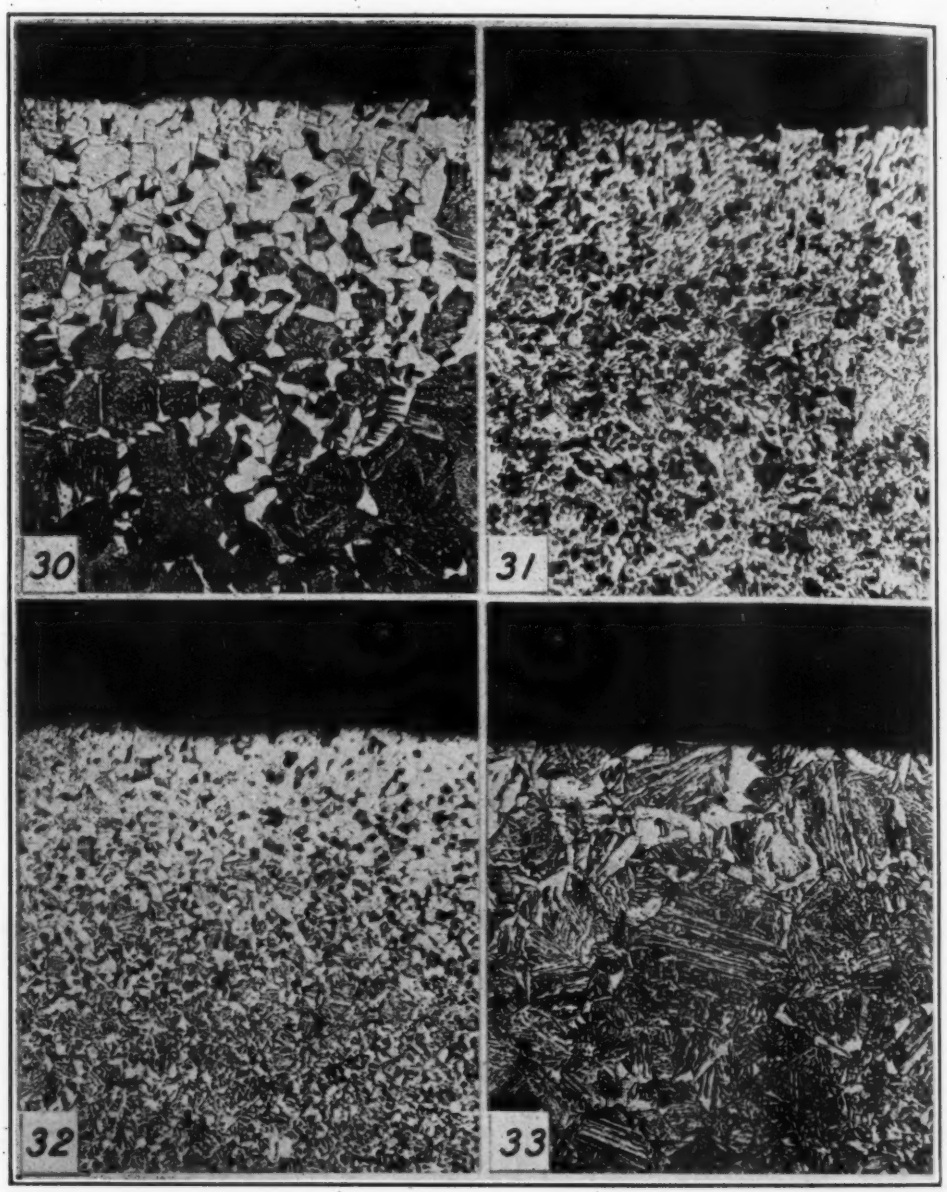


Fig. 30—Surface heated to 1800 Degrees Fahr. for 4 hours (1700 Degrees Fahr. similar) Decarburization Partial. × 100.
Fig. 31—Surface of S. A. E. 4130 heated to 1400 degrees Fahr. for 4 hours. × 100.
Fig. 32—Surface of S. A. E. 4130 heated to 1600 degrees Fahr. for 4 hours. × 100.
Fig. 33—Surface of S. A. E. 4130 heated to 1800 degrees Fahr. for 4 hours. Partial decarburization. × 100.

980 degrees Cent.) in intervals of 100 degrees Fahr. (40 degrees Cent.). The specimens were machined from ¾ inch round bar stock to ½ inch round by 1 inch, thus insuring a starting surface free from decarburization. These were placed in an electric fur-

nace and held for two and four hour periods at the temperatures mentioned. The results show a marked and total decarburization to occur in the chromium-aluminum-molybdenum analysis at 1500 and 1600 degrees Fahr. (815 and 870 degrees Cent.). Below these temperatures at 1400 degrees Fahr. (760 degrees Cent.) no decarburization occurred, while above at 1700 and 1800 degrees Fahr. (925 and 980 degrees Cent.) there occurred a partial decarburization and heavy scaling. This indicates that at the latter two temperatures the steel was scaling faster than the carbon was migrating to the surface. The S.A.E. 4130 steel shows comparatively little decarburization up to 1600 degrees Fahr. (870 degrees Cent.) and a small partial decarburization above this temperature. Photomicrographs shown in Figs. 28 to 33, inclusive, show the decarburizing effect of the four hour heating period at temperatures 1400, 1600 and 1800 degrees Fahr. (760, 870 and 980 degrees Cent.).

It is quite important to know the depth of the decarburized area on heat treated forgings and bar stock in order that the proper size may be used to insure its removal by machining and grinding. While in most cases sufficient stock is removed in machining operations to eliminate the decarburized surface, these facts should, nevertheless, be kept in mind.

Brittleness and Its Elimination

Is the nitrided case brittle? And how can it be tested to show brittleness? In view of the high surface hardness attained in nitriding, these questions constantly arise. The first question is, indeed, a relative one and can be answered one way or the other depending upon the service conditions. For example, if the case is subjected to a too heavy impact where the supporting core material is upset, then the case will fail and may be termed brittle. Again, if the load is not heavy and well under the elastic limit of the core, then with a properly nitrided case no brittleness is encountered. The fact that nitrided camshafts, valve tappets and wrist pins are working successfully is evidence to the latter statement.

To determine if the case is brittle, two tests have been applied. The first is to take a Vickers hardness reading on the nitrided surface after polishing with emery cloth. Under this condition a brittle case will spall or flake off while a non-brittle case will

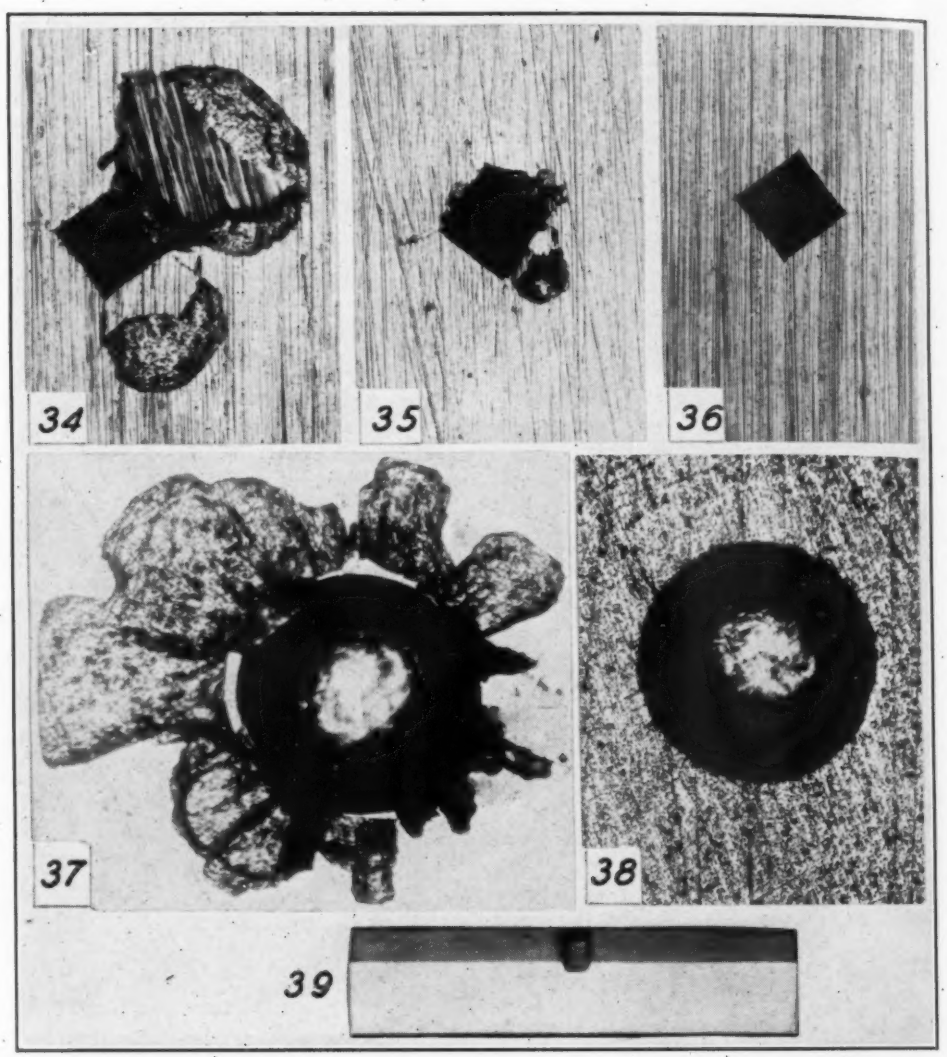


Fig. 34—Vickers Reading of Brittle Case Showing Spalling. × 100.
Fig. 35—Vickers Reading of Slightly Brittle Case. Slight Spalling. × 100.
Fig. 36—Vickers Reading of Tough Properly Nitrided Case. × 100.
Fig. 37—As Nitrided. Showing Rockwell "no load" Impression Causing Marked Spalling. × 100.
Fig. 38—Same Surface as in Fig. 37 but Reheated to 1200 degrees Fahr. under Iron Filings before Making Rockwell "no load" Impression. × 100.
Fig. 39—Humphrey Slow Bend Test with Round Notch.

show a clean cut impression. Photomicrographs taken of Vickers reading on brittle and non-brittle cases are offered in Figs. 34, 35 and 36. All of these cases were approximately 1000 Vickers Brinell.

A still more drastic test is that of taking a Rockwell "no load" reading on similar surfaces. By Rockwell "no load" is referred to using the Rockwell machine with diamond cone but removing the usual 150 kilogram weight. In this condition the load on the

diamond is 60 kilograms. With this test, brittle cases will show much spalling, while the non-brittle case will not spall but may show some few radial cracks. Photomicrographs in Figs. 37 and 38 show brittle and non-brittle cases.

A further study was made to determine, if once a brittle case is formed, what methods convert it to a non-brittle case. A specimen known to be brittle was reheated at increasing temperatures starting from 1000 degrees Fahr. (540 degrees Cent.). Fig. 37 represents the reading taken on the Rockwell "no load" before any reheating. The specimens were reheated under iron filings to keep the surface from scaling. The reheating temperatures 1000 and 1100 degrees Fahr. (540 and 595 degrees Cent.) had little or no effect in removing the brittleness. At 1150 and 1200 degrees Fahr. (620 and 650 degrees Cent.), however, the brittleness was completely gone. Fig. 38 is the reading taken after the 1200 degrees Fahr. (650 degrees Cent.) reheating.

With this in view, nitriding cycles were run in which the specimens were nitrided for varying periods of time at 975 degrees Fahr. (525 degrees Cent.). At the end of this period the temperature was raised to 1180 degrees Fahr. (580 degrees Cent.) and held in one case for five minutes, in another for two hours and still another for 40 hours before cooling to the low temperature of 300 degrees Fahr. (150 degrees Cent.), when specimens were removed from the nitriding furnace. In all such cases the surface hardness was above 900 Vickers Brinell and a non-brittle case obtained. It will be recalled in Section I of this paper that reheating to 1200 degrees Fahr. (650 degrees Cent.) had only slight effect in lowering the hardness of the nitrided case. Again in Section II it was noted that the structure of the case nitrided at 1200 degrees Fahr. (650 degrees Cent.) indicated diffusion was occurring. These two facts explain in part the observed facts that a heating to 1180 degrees Fahr. (1150-1200 degrees Fahr.) on the end of a nitriding cycle increases markedly the toughness of the case with little or no sacrifice in hardness.

That nitrided parts, such as spindles and camshafts, can be straightened cold, if warped slightly, is a proven fact. An interesting test, that shows this is to be expected, was made on the Humpfrey slow bend machine. In this test, nitrided chromium-aluminum-molybdenum steel was compared to carburized and hardened steels. The carburizing analyses were 5 per cent nickel steel

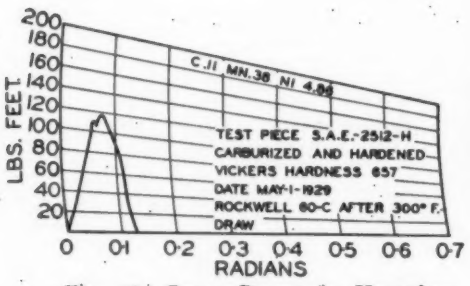


Fig. 40—Curve Drawn in Humpfrey Slow Bend Test on S. A. E. 2512 Steel.

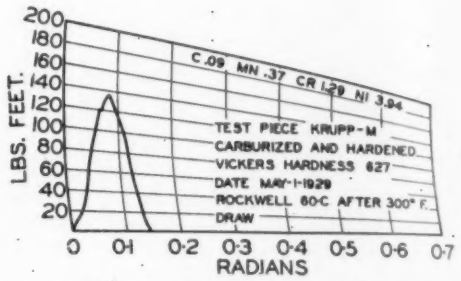


Fig. 41—Curve Drawn in Humpfrey Slow Bend Test on Krupp Analysis (Cr-Ni).

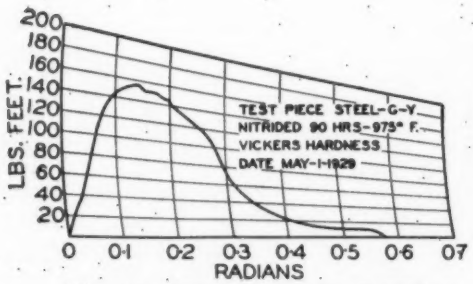


Fig. 42—Curve Drawn in Humpfrey Slow Bend Test on Chromium-aluminum-molybdenum Steel. As Nitrided.

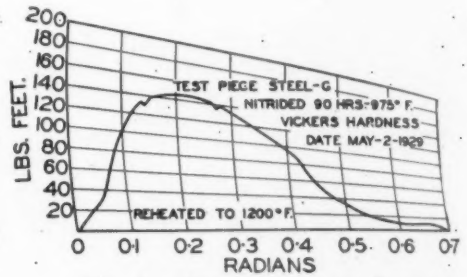


Fig. 43—Curve Drawn in Humpfrey Slow Bend Test on Chromium-aluminum-molybdenum steel. Nitrided and reheated to 1200 degrees Fahr.

and Krupp and were selected as these are the toughest of the carburizing grades. These were carburized for 8 hours at 1650 degrees Fahr. (900 degrees Cent.) and then hardened.

Fig. 39 shows the type of test specimen used with its round notch to minimize strains set up in quenching of carburized specimens. The Humfrey machine draws a stress-strain diagram and gives the amount of energy or work expended in the breaking of the specimens. Figs. 40-43, inclusive, show the curves obtained by the various analyses on the Humfrey machine. The chromium-aluminum-molybdenum specimens have taken a greater bend before the first failure of the case than have the carburized specimens. This, it is believed, explains why nitrided parts may be straightened if they are but slightly warped. In the case of the nitrided specimens, the one reheated to 1200 degrees Fahr. (650 degrees Cent.) after nitriding shows a greater bend and a greater area of work done, indicating a greater toughness of case.

Summary

1. Early nitriding analyses were chromium-aluminum, chro-

mium-nickel-aluminum, and, later, chromium-aluminum-molybdenum. A lowering of the chromium and aluminum content of latter analysis has produced the present nitriding analysis.

2. Hardness gradation charts of chromium-aluminum-molybdenum versus case hardened S.A.E. 6115 and 4615 show the nitrided case to be much the harder (up to a case depth of 0.030 inch in this instance).

3. In reheating the hardened nitrided and carburized cases from 70 to 1200 degrees Fahr., the nitrided case suffers little or no loss in hardness, while the carburized case falls off in hardness progressively with increase in temperature.

4. At nitriding temperatures of 1000, 1100 and 1200 degrees Fahr. (540, 595 and 650 degrees Cent.), given 50 liters per hour as a standard flow, an increase in rate of flow produces increase in hardness and penetration. At 950 degrees Fahr. (510 degrees Cent.), increase in flow has but little effect.

5. At the extreme surface a decarburization is taking place; this is proven by nitriding and analyzing for carbon, of fine chromium-aluminum-molybdenum steel drillings.

6. The structure of the case varies but slightly until a nitriding temperature of 1200 degrees Fahr. (650 degrees Cent.) is employed, when a more uniform structure is observed, indicating better diffusion.

7. For a given nitriding temperature an increase in flow does not alter the case structure.

8. That chromium and aluminum contents under 1 per cent give satisfactory hardness is indicated.

9. The effect of nickel has been shown in combination with chromium and aluminum, also with molybdenum and aluminum.

10. Two "duplex nitriding cycles" investigated suggest the nitriding first at a low temperature (950 degrees Fahr.) and follow by nitriding at a high temperature (1180 degrees Fahr.) should give best results.

11. The subject of decarburization is discussed in detail, showing susceptibility of chromium-aluminum-molybdenum steel to decarburize and effect of nitriding a decarburized surface.

12. Brittleness—methods of determining brittleness are discussed. To eliminate brittleness a heating to 1150-1200 degrees Fahr. (620-650 degrees Cent.) at the end of the nitriding cycle is recommended.

ACKNOWLEDGMENT

The author wishes to thank H. Dittmar for most of the photomicrographs and H. J. Deal for his aid in taking and plotting of the hardness charts.

The cooperation and assistance of J. W. Harsch of the Leeds and Northrup Co. for running some of the nitriding cycles are gratefully appreciated.

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DISCUSSION

Written Discussion: By J. P. Walsted, Massachusetts Institute of Technology, Cambridge, Mass.

In any metallurgical process as new as nitriding, many researches must be carried out before we reach a complete understanding of all the details. Mr. Sergeson's paper is of great value in furnishing us additional information.

Mr. Sergeson has used the Vickers machine in making his hardness determinations. While this machine is, no doubt, very satisfactory for most work, I believe that the Herbert pendulum or Shore Monotron would be a more satisfactory instrument in this research. The Vickers machine has the disadvantage that considerable penetration is obtained, thus giving not the surface hardness but an average of the hardness between the surface and the penetrated depth. It would be of interest to see the hardness tests repeated using the Herbert pendulum.

The author has raised the question of using a tube furnace for nitriding. Dr. Homerberg and I have used tube furnaces for experimental nitriding with excellent results. The few occasions when poor results were obtained were in each case traced to the steel used. Where small machine parts have been sent in for nitriding, there has been in a few cases a mistake in the selections of the steel. In our own research work where we selected our own steel, no difficulty was encountered. The subject of decarburization is of great importance in nitriding. There is no doubt that nitriding of a decarburized surface will produce a spalling case. Decarburization that occurs in the nitriding furnace is, however, not as easily detected. The thin white layer found at the surface of a nitrided specimen is, I believe, the same material that is sometimes found in the grain boundaries and cleavage planes. X-ray patterns of a powder, nitrided at 950 degrees Fahr. for 48 hours, show a constituent which is neither alpha nor gamma iron. I believe this material to be a nitride. In nitriding fine materials there is so much surface exposed that the nascent hydrogen has a better chance to cause decarburization which explains Mr. Sergeson's results obtained by analysis. A solid specimen does not present the same amount of surface and the reaction must necessarily be much less rapid. If decarburization takes place to any appreciable extent in nitriding a solid specimen, the case should spall. Moreover, the white layer reacts to heat tinting and sodium picrate etch in such a way as to indicate that it is a nitride rather than ferrite.

It is gratifying to see that Mr. Sergeson has made a study of the influence of the composition of the steels used in nitriding. Too little attention has been given to this phase of the subject in the past. An aluminum content below 0.70 per cent is shown to be less satisfactory than a higher content. I favor an aluminum content of about 1.0 per cent to insure good results. I would like to see photomicrographs and service results before I would accept a nitriding steel of aluminum content as low as 0.50 to 0.70 per cent. It is well known that steels with low aluminum content are liable to show needles on nitriding.

Mr. Sergeson is to be complimented on his excellent contribution to the subject of nitriding.

Written Discussion: By H. W. McQuaid, Timken-Detroit Axle Co., Detroit.

This paper of Mr. Sergeson's shows clearly the advantage of the nitrided case over the carburized case as far as the depth-hardness curves indicate. We find, in making comparative transverse tests, that the

nitrided case is apparently not as strong in tension as is a carburized case. It is believed that further investigations may show that the nitrided case has comparative strength with the carburized case, as the investigations we have made to date have covered only a small number of samples. There are several points in this paper which are of considerable importance to the practical nitrider. It is demonstrated that increasing the flow of ammonia at the higher temperature results in increased hardness and penetration. This is another way of saying that decreased dissociation is an

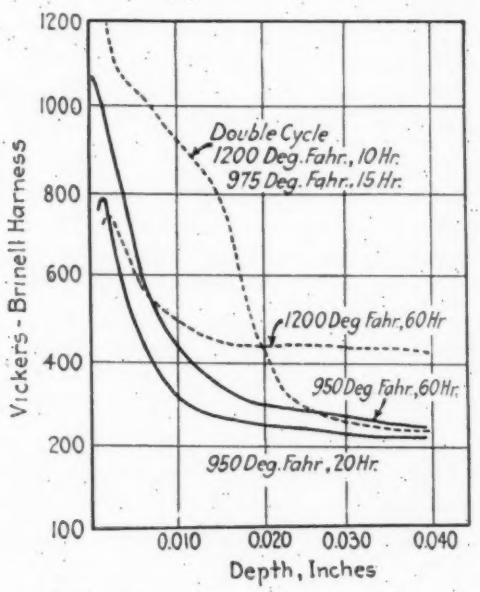

Fig. 1—Hardness-Depth Curves for Nitrided Cases Made Under Different Conditions.

advantage, and that since the dissociation increases with the temperature above 950 degrees Fahr., increasing the flow would have a greater effect as the temperature is increased above 950 degrees Fahr. This is particularly true in the type furnace shown in Fig. 7 where the dissociation decreases rapidly, and is practically complete at 1200 degrees Fahr. It is also shown that decarburization accompanies the nitriding operation, and is apparently due to the action of the hydrogen. It is also shown that decarburization is associated with brittle cases, which is checked by practically every investigator. In each case, however, the brittle case is also indicated by a coarse decarburized structure and inter-crystalline penetration of the nitrides. We have found that total decarburization, and especially when accompanied by coarse grain net-work, is brittle after nitriding; but that the brittleness is not due to the low carbon content but to the coarse grain and the most satisfactory nitriding steels, from a machining standpoint, should be those which contain the minimum carbon necessary to permit the retaining of a fine sorbitic structure.

One of the most valuable contributions in this paper is the curves

showing the satisfactory results which can be obtained with lower aluminum and chromium contents than at present specified for nitriding steel. In most cases where the hardness of the case is the important criterion and the core strength would be satisfactory, the use of less alloys and lower carbon would certainly be more beneficial in the making and fabricating of the nitriding steel.

It is shown that the duplex nitriding cycle using a low temperature (950 degrees Fahr.) followed by a higher temperature (1180 degrees Fahr.) should give good results and that the reversal of this cycle is not so satisfactory. It is believed by the writer that the success which is to be obtained with the duplex runs depends to a great extent upon the dissociation in the nitriding retort. In the type furnace of Fig. 7 where the dissociation is high at the higher temperature as is shown by Fig. 25, it is very difficult to build up a satisfactory hardness at the higher temperature, so that the diffusion results in a relatively soft case. With high dissociation, the concentration of hydrogen is such that the nitriding action is either stopped, or perhaps the cycle may be even reversed and the nitrides reduced. If a comparison is made between Fig. 11 and Fig. 25, it will be found that the 950 degrees Fahr. run for 48 hours is considerably better than the duplex run; indicating that the time element is the most important in this case. The curves shown do not compare with some of the results obtained by the writer when operating on a duplex cycle in a retort type furnace. Fig. 1 of this discussion shows the depth-hardness curves of a duplex run made at the Timken plant, operating as shown.

In this run, the dissociation at 1200 degrees Fahr., was maintained at 30 per cent, and at 975 degrees Fahr., at 15 per cent. I am convinced that a great deal of work can be done in working out a cycle of temperatures, pressures, etc., with proper dissociation control to give us a control of the nitriding case which would be satisfactory to the most critical.

The recommendation that the nitrided piece be heated to 1200 degrees Fahr., at the end of the cycle to eliminate brittleness should be of the greatest practical importance, and will no doubt be investigated thoroughly by most nitriding plants.

W. J. Merten: I wish to discuss this paper from a practice standpoint. My first impression in studying the method of processing he employed was to wonder whether it was intended to quench harden in ammonia rather than to nitride with ammonia. 500 litres of ammonia entering as is shown midway up on the right side of the furnace chamber in sketch Fig. 7 and taken off at the same level on the left must have a decided cooling effect on the work, which is obviously not indicated by the thermocouple placed in the bottom of the furnace below the fan blades so that any nitriding results based upon data so obtained are at least questionable.

The design of a furnace with respect to entrant and exit piping for ammonia so as to create a natural flow from bottom to top across the furnace is certainly advisable and good practice. The paddle wheel or fan as a factor in Sergeson's processing in this respect is rather doubtful on account of the rather high pressure.

Judging from the picture, Fig. 7, it appears as if the exit pipe opening is larger than the continuous entrant pipe opening, my own experience indicates this to be another factor to be guarded against, a slight pressure created within the nitriding container for intimate contact and avoidance of stagnant gas pockets is quite essential for best results.

If as is indicated by Mr. Sergeson's work and suggested by him, it is necessary to use a blast of ammonia through a nitriding furnace for 90 hours to keep dissociation down to extremely low percentages to avoid hydrogen packing on the surface and practically employ the larger percentage of the ammonia to cool the furnace chamber, nitriding will never be practical nor economical. It was for the reasons stated above that the Westinghouse Electric and Manufacturing Company developed a practice based upon the molybdenum-aluminum nitriding alloy steel in which practice greater depth than the 90 hour cycle and better hardness and less brittleness is obtained in a 20 hour cycle. This obviously indicates that chromium and nickel are objectionable alloying elements. It is here where a large amount of interesting work awaits the careful investigator for the advancement of nitriding of alloy steel.

Author's Closure

I wish to thank Mr. Walsted for his sincere discussion of this paper. Some of the statements made in this discussion are not in agreement with ours and will be discussed in order presented.

The Herbert pendulum does not have the flexibility or speed of operation that the Vickers machine has. With a surface hardness of 1000 Vickers Brinell the depth of the impression made by the Vickers diamond pyramid is 0.001 inch. Five or more such readings may be obtained in succession on a taper-ground specimen (as explained in paper). These two facts do not indicate that considerable penetration is obtained when using the Vickers machine. The curves are comparable and little would be gained by repeating same using the Herbert pendulum.

The thin white layer can be readily detected as specimens are ground on the 3-degree taper and the polished tapered sections examined in the etched condition at high magnification ($\times$ 850).

I cannot see where there should be any difference in reaction between the nascent hydrogen on the carbon of the drillings and of a solid specimen. It is true that there is greater surface of the drillings exposed and the decarburization should proceed faster but decarburization should also take place to a lesser extent on the surface of the solid specimen. If we introduce benzene (C_6H_6) into the nitriding chamber when nitriding at 950 degrees Fahr., the decarburization of the drillings is prevented and we have not observed the white area on the surface of solid specimens. At higher temperature, 1000 degrees Fahr. and above, even the benzene is ineffective in preventing surface decarburization. The white area containing approximately 7.45 per cent nitrogen may be a nitride or a series of nitrides. Its constituents are, however, ferrite (iron plus elements in solution with the iron) and nitrogen.

It has not been observed that the low aluminum contents are susceptible

to the showing of nitride needles. Our experience shows that the condition of the carbon determines the amount of nitride needles present. A sorbitic structure shows no needles while as the presence of free ferrite increases, so the nitride needles increase.

There is one subject of Mr. McQuaid's very able discussion that I should like to discuss further. That is the explanation as to why we must run duplex cycles starting first with the low temperature (950 degrees Fahr.) and follow with the higher temperature (1200 degrees Fahr.).

The specimens A, B, C and D of heat 3305, previously mentioned, after having had hardness values taken on the 3-degree taper were re-nitrided to

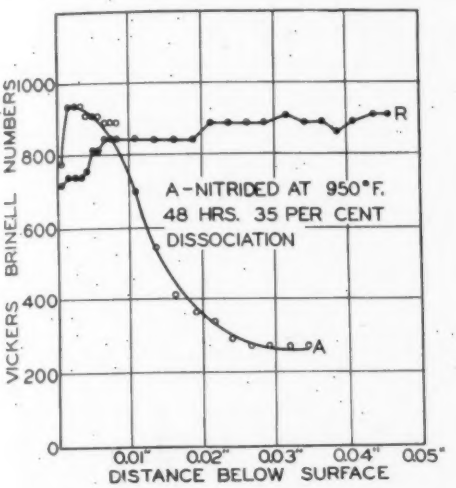

Fig. 1A

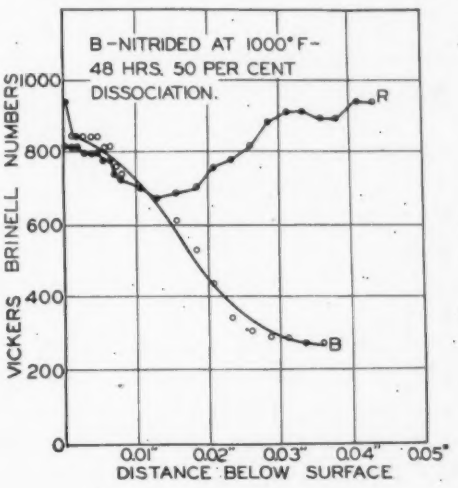

Fig. 1B

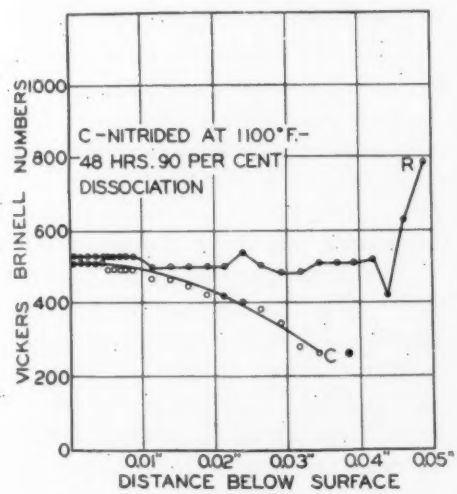

Fig. 1C

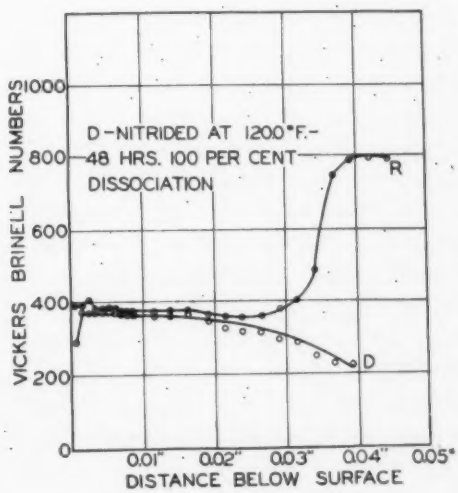

Fig. 1D

Figs. 1A, 1B, 1C and 1D—Showing Effect of Re-Nitriding on the Taper-Ground Surface of Specimens Previously Nitrided at 950, 1000, 1100 and 1200 degrees Fahr. respectively, before being Taper Ground.

note the hardness effect on the freshly ground 3-degree taper. All specimens A, B, C and D were re-nitrided at 975 degrees Fahr. for 48 hours with 26 per cent dissociation and hardness values again taken on the tapered surface. The results are shown in Figs. 1A, 1B, 1C and 1D and present interesting data. These curves point to the following:

1. That material nitrided at 1100 and 1200 degrees Fahr. show relatively low surface hardness which cannot be raised by subsequent nitriding at a lower temperature. Thus showing why close regulation of temperature is essential.

2. They point out why the duplex cycle must start at the low temperature first for obtaining a high surface hardness.

3. They suggest that any material nitrided under 1000 degrees Fahr. showing soft spots due to poor circulation of gas can be re-nitrided to produce high surface hardness.

4. At 1000 degrees Fahr. there is a slight tendency to follow the original hardness curve.

5. That after nitriding at 1100 or 1200 degrees Fahr. the entire case must be removed in order to obtain a high surface hardness on subsequent nitriding at lower temperature (950 to 975 degrees Fahr.).

The above work was done in the type of furnace shown in Fig 7 of the paper.

In reply to Mr. Merten may I say in the outset that his discussion seems to have lost the point that to investigate the effect of flow of ammonia gas it was necessary to use wide variations in flow.

The circulation of gases in the furnace is very rapid and their path passes the thermocouple. The thermocouple is bare and very sensitive to any change in temperature. Again there is sufficient metal within the furnace as well as the heating elements themselves to prevent any decided cooling effect. The rapid circulation caused by fan revolving at 1750 revolutions per minute makes the entrance and exit locations of the gases relatively unimportant as there is no chance for any stagnant gas pockets. The exit pipe must be larger than the entrance because as oil is used as a seal there must be no back pressure; the gas must be free to escape. Specimens taken from top-middle-bottom at center and side show that uniformity of hardness and penetration is obtained.

In Mr. Merten's fourth paragraph he has certainly misconstrued my statements. In no case have I recommended a 90-hour cycle using a blast of ammonia (a rather indefinite figure)—which I presume he means using the high temperature of 1200 degrees Fahr. Nitriding is now on an economical basis with the nitriding temperatures running from 950 to 975 degrees Fahr. and time limits of 10 to 90 hours, depending upon requirements. With the low temperatures, low rates of ammonia flow can be and are used. Higher temperatures require higher rates of flow but give more rapid penetration, hence decrease time limit.

While I appreciate Mr. Merten's criticisms, I would like him when making comparisons to give actual figures on hardness, case depth, analysis, time, flow, etc., for this would enable a check of his results by anyone interested.

SHORT-TIME NITRIDING OF STEEL IN MOLTEN CYANIDES

By A. B. Kinzel and J. J. Egan

Abstract

This paper describes a new development in nitriding whereby a very hard thin case is obtained on articles made of vanadium or aluminum nitriding steel by immersion for two hours at 860 degrees Fahr. (460 degrees Cent.) in a specially developed salt bath. This bath consists of a low-melting solution of potassium and sodium cyanides. Tests show that this case is as hard as that obtained with the usual long-time ammonia treatment. Moreover, it has the same wear resistance and corrosion resistance although the ability to withstand high local stress is less than with a thicker case.

Introduction

THE process of nitriding is receiving much attention from the industrial world at the present time as the properties of the nitrided material are attractive for many applications. Nitriding is usually accomplished by subjecting the material to the action of ammonia at elevated temperatures. It is generally believed that best results on hardness and ductility of the case are obtained with temperatures below 500 degrees Cent. (930 degrees Fahr.) although some investigators report satisfactory results at higher temperatures. The time of nitriding varies with the individual method and purpose from 18 to 90 hours. Such a time-consuming process is difficult to fit into the modern high-speed production schedule and entails considerable equipment per unit of production. The depth of the case in the above process varies somewhat with the time but the authors find that when the time is reduced below approximately ten hours no extremely hard case results with the usual methods and nitriding steels.

The advantages of a nitrided case are great hardness, corrosion resistance and lack of distortion of the specimen in the process. In

The authors, members of the society, are associated with the Union Carbide and Carbon Research Laboratories, Inc., Long Island City, N. Y. Manuscript received May 31, 1929.

many instances where rubbing wear is involved, surface hardness only is required and failure to resist local high stresses at the surface is not important. Moreover, in many such applications wear of even as little as 0.0005-inch would be so serious as virtually to constitute failure of the part. In the carburizing field if high local stresses are to be met, a deep case is used but there are many applications where a thin case is satisfactory. Such a case is often produced by treating at temperatures in the vicinity of the carbon-iron critical range in a salt bath containing cyanides. It has long been recognized that while the major effect in this process comes from carbon, nitrogen plays an important part.

It occurred to the authors that an extremely hard and very thin case, having all the advantages and properties of the usual nitride case with the exception of ability to withstand local high compression stress, would fill a real need, provided it could be produced in a short time. Such a case has not been obtained in a short time with the simple ammonia treatment so other nitriding agents were considered.

Requirements for a Nitriding Medium

In accordance with previous results obtained at these laboratories, it was decided that such a nitriding agent should operate at temperatures approximating 460 degrees Cent. (860 degrees Fahr.) for the best results. In order to have high concentration of liberated nitrogen in contact with the steel, liquid rather than gaseous media were considered. It was also believed that the presence of free oxygen or hydrogen was detrimental to nitriding. The problem thus reduced itself to the use of a nitrogen-liberating salt which contained no oxygen and preferably no hydrogen and which would melt at sufficiently low temperatures to allow the process to be carried out at the optimum nitriding temperatures. No such single salt was found although the cyanides, particularly those of sodium and potassium, approached these requirements.

Properties of Molten Cyanides

Pure sodium cyanide melts at 560 degrees Cent. (1040 degrees Fahr.) and pure potassium cyanide at 601.2 degrees Cent. (1114 degrees Fahr.) These temperatures were deemed too high for satisfactory nitriding conditions. With the potassium cyanide, the process would have to be carried out above the nitrogen-iron eutectoid

point and with the sodium cyanide the temperature is too close to this point for satisfactory operation in production. Moreover, the authors find that more satisfactory cases are in general obtained at temperatures approximating 460 degrees Cent. (860 degrees Fahr.) than at the upper limit of the sub-critical zone. Accordingly, work on lowering the temperatures of these cyanides by suitable combinations or additions was undertaken. The liquidus and solidus lines resulting from the combination of the potassium and sodium cyanides were determined and a low-freezing solution was noted at about 445 degrees Cent. (835 degrees Fahr.) This consists of approximately 53 per cent sodium cyanide and 47 per cent potassium cyanide. A bath of this mixture was made up and tested for fuming, as the undesirable fuming quality of this salt is well known. No measurements of the vapor pressure of the salts were made but it was definitely established that at 460 degrees Cent. (860 degrees Fahr.) the vapor pressure is low enough so that operation can be carried out comfortably without a hood although as a matter of general application a hood has been used.

Nature of the Case Produced

The nitriding properties of the bath were tried on the vanadium steel developed by one of the authors. The specimen used analyzed 0.20 per cent carbon and 0.5 per cent vanadium. It was found that a two-hour treatment at 460 degrees Cent. (860 degrees Fahr.) resulted in a very hard corrosion resistant case. The depth of this case is of the order of 0.0005-inch. Measurements on the hardness of the case made with a microcharacter showed 18,000,000 K units, a value three times as hard on the microcharacter scale as the 6,000,000 K units obtained on the surface of the usual 70-hour ammonia-treated specimens of the same steel. Similar results were obtained on an aluminum-bearing nitriding steel. Impact tests were performed on cyanide-treated, chromium-vanadium, nitriding steel specimens in comparison with the ammonia-treated and untreated specimens of the same steel, the nitriding being carried out after the notch was cut on the impact specimens. These specimens had been previously oil-quenched and tempered at 460 degrees Cent. (860 degrees Fahr.) for one hour. The results are as follows:

Nitriding Medium	Temperature	Time	Izod
Untreated			67 foot-pounds
Ammonia	460° Cent. (860° Fahr.)	70 hours	10.5 foot-pounds
Molten Cyanides	460° Cent. (860° Fahr.)	2 hours	61 foot-pounds

The figures show that the order of ductility of the specimen is unaffected by the cyanide treatment and that the thin case does not cause cracks which are propagated through the material under stress. Peening tests were tried on the cyanide-nitrided case without chipping or cracking and impressions with a 10-millimeter ball were made without cracking of the case, probably due to its lack of thickness and high elastic limit.

Tensile tests on another chromium-vanadium nitriding steel before and after cyaniding gave the following results on specimens which had been previously oil-quenched and tempered at 600 degrees Cent. (1110 degrees Fahr.) for one hour.

Medium	Ultimate Strength pounds per square inch	Per Cent Elongation in 2 inches	Per Cent Reduction in Area
Untreated	146,000	20	61
Molten Cyanides	144,000	17	51

In order to test further the characteristics of the case a piece of ¾-inch shafting which had been nitrided in molten cyanides was rotated in a wear testing apparatus. This consists essentially of an open cylinder filled with rusty water, the water being agitated by means of a paddle wired to the shaft under test. The shaft proper extends into the cylinder through a stuffing box which is adjusted so that there is a very slight leak of rusty water. It is readjusted as necessary. Ordinary machine steel shafting tested in this apparatus showed serious failure due to wear and general corrosion on inspection after 17 million revolutions. The nitrided specimen showed no sign of wear after 66 million revolutions and the material was entirely free from corrosion.

It was assumed that the hard case was produced essentially by nitrogen rather than carbon as in the higher-temperature cyanide treatments. The hardness produced without quenching appeared to confirm this view. To obtain further evidence, vanadium nitriding steel was rolled to sheet 0.006-inch thick and treated for two hours at 460 degrees Cent. (860 degrees Fahr.) in molten cyanide. Carbon and nitrogen analysis on the material as rolled and as nitrided gave the following figures:

	Carbon Per Cent	Nitrogen Per Cent
As rolled	0.29	0.002
Cyanide treated	0.32	0.0705

Moreover, on treating plain carbon steels no case resulted.

The color of the case is dark except when special precautions are taken to clean the material before nitriding and to cool with an adherent film of the salts. This film may be readily washed off.

Variations of the Process

Work on the time of nitriding in the cyanide bath showed that no increase in depth or hardness of the surface was obtained by nitriding longer than two hours. Attempts were made to dilute the bath and note the effect on the nitriding. However, the diluents, which comprised the more stable salts such as chlorides of sodium or barium, raised the melting point too much if added in appreciable quantities and those having a low melting point volatilized too readily from the bath. Various commercial tempering salts were examined as possible diluents. These were found to contain nitrites or nitrates that were unstable in the presence of cyanides while their oxygen content rendered them unfit for this purpose.

Conclusions

Nitriding in a molten bath of a mixture of potassium and sodium cyanide at temperatures low enough to prevent distortion produces a case harder than the usual case produced with ammonia and about 0.0005-inch thick in two hours.

The combination of hardness and corrosion resistance should make articles treated by this process suited to a great many applications even though the case is quite thin.

Acknowledgment

The authors wish to express their appreciation of the interest and stimulation given by Mr. F. M. Becket, president, and Mr. J. H. Critchett, vice-president of the Union Carbide and Carbon Research Laboratories, as well as the general assistance rendered by their colleagues at the laboratories.

DISCUSSION

Written Discussion: By V. O. Homerberg, Massachusetts Institute of Technology, Cambridge, Mass.

The uses for material having such a shallow case will be limited to applications where a superficial layer of great hardness is sufficient and

where a combination of superficial hardness with resistance to corrosion is desirable.

I do not believe that the authors intended to convey the impression that the case produced by their method was actually three times as hard as the one produced by a 70-hour treatment with ammonia gas when applied to the same nitriding steel, although such a statement was made as the result of determinations with the micro-character. The surface hardness of ammonia-treated aluminum-chromium steel is over 1000 Brinell. It is inconceivable that the surface hardness of the cyanide-treated material is over three times this value.

Exception is to be taken to the statement that no extremely hard case can be obtained by the usual method of nitriding steel with an ammonia exposure below approximately ten hours. I have nitrided hundreds of parts in less time than ten hours with excellent results with respect to surface hardness. At least one manufacturing company is commercially nitriding large parts by using an ammonia exposure not exceeding this number of hours. A modification of the regular nitriding process is used in this plant.

I hope that the authors will make additional experiments in which higher temperatures will be used to obtain a deeper case.

The pure cyanides of sodium and potassium were used in making the salt baths. If this method is to be applied commercially cyanides containing various impurities will be used. A study should be made, therefore, to determine the effect of the impurities present and to determine the percentage of the commercial forms of the cyanide to be used in order to obtain the proper salt bath for the purpose.

A salt bath for nitriding has certain advantages as well as disadvantages over the ammonia treatment. I hope that the authors will contribute further information to this important subject.

Written Discussion: By C. B. Sawyer, Brush Laboratories, Cleveland.

The paper by Messrs. Kinzel and Egan seems to me of great importance. From it we learn that nitride hardness of very large magnitude is obtained; that the time required for producing it is small; that the method employed promises great convenience.

Also, for the theory of nitriding a most significant statement occurs in their paper on page 179 as follows: "Moreover, on treating plain carbon steels no case resulted." This statement applies evidently to a comparison between nitriding steels and plain carbon steels when treated in the cyanide bath. The statement is of interest because both these steels are nitrided at this temperature by ammonia, and the cyanide bath is accordingly indicated as being less powerful than an ammonia gas stream.

In other words, the cyanide bath does not seem able to produce sufficient nascent nitrogen pressure to force nitrogen into solid solution with ferrite, but the nitriding steels seem to have an element in solid solution in ferrite which might be said to draw nitrogen into solution from the bath. The cyanide bath can then become effective.

Aluminum has been shown to have a great affinity for nitrogen.

When aluminum has entered into solid solution with ferrite it probably not only tends to draw nitrogen into such solution with it, but also seems to hold it there, apparently preventing the precipitation of nitride. Aluminum effectively may increase the solubility of nitride in ferrite.

The man who seems first to have observed this action of aluminum was Tschischewski,[1] in 1915. He studied nitrides of manganese, silicon and aluminum. These were increasingly stable in the order named. Aluminum nitride was not decomposed even at 3180 degrees Fahr. (1750 degrees Cent.). As a result of his observations, Tschischewski stated as follows: "These experiments prove that aluminum added to molten steel combines with nitrogen and forms with it a hard solution of aluminum nitride without evolving any nitrogen."

Written Discussion: By H. W. McQuaid, Timken-Detroit Axle Co., Detroit.

Mr. Kinzel indicates another method of attack on nitriding. The results he gets are comparable to those obtained in treating plain carbon steel for approximately 16 hours at 1100 degrees Fahr., in ammonia. Practically the same results are being obtained in daily practice by us in plain carbon steel in ammonia for this length of time. The advantage of obtaining such a case in two hours would, of course, be obvious. At the same time, there is some doubt in my mind as to the practicability of handling and maintaining such a bath as is described. One of the disadvantages would be the expense of maintaining the bath due to the carrying away of the cyanide by the work. Apparently, however, since no hood is necessary, the bath is stable and there is no reason why practical operation should not be obtained.

I believe, as does Mr. Kinzel, that the presence of free oxygen or hydrogen above a certain minimum is detrimental to nitriding and that the use of a medium free from these elements would be very desirable. I do not believe, with ordinary steels including the nitriding series, that it is necessary to work at such a low temperature as 850 degrees Fahr., and I am certain that an investigation along this line would be of considerable practical value.

Authors' Closure

Dr. Homerberg expresses disappointment at the depth of the case obtained. The authors, however, feel no such disappointment but rather are very pleased with the case obtained. The process is a new one and we had no reason to believe that it would be successful, thus the case of one-half thousandths thick, with a hardness some three times that of the usual nitrided case, was a most gratifying result. It is true that the application is somewhat limited, due to the depth of the case, but we feel, nevertheless, that a broad field is open to this application.

Dr. Homerberg brought up the matter of case hardness. As stated in the paper, on the micro-character scale the hardness of the case produced in molten cyanides is three times that produced in the 70-hour

[1] *Journal*, Iron and Steel Institute 1915.

ammonia treatment. No attempt has been made to convert this to Brinell scale, but were such a conversion to be made, it would seem to me to be just as logical to call this 3000 Brinell as to call the ammonia case 1000 Brinell. Neither figure is actually obtained on the Brinell machine. We have no absolute measure of hardness, so that depending upon the particular yardstick used, a figure of any order may result. The fact remains, however, that the hardness of this case is certainly very much greater than that of the ammonia treated material.

Regarding the matter of higher temperatures. Additional experiments have been made and, although a deeper case is obtained, the hardness of the case drops off very rapidly after the temperature is increased. Since the original experimental work was carried out, considerable nitriding has been accomplished with technical grades of sodium potassium cyanides, without any deleterious effects on the resulting case.

Regarding the nitriding of steel in ammonia at exposures opproximating ten hours, mentioned by Dr. Homerberg. It has been the writer's experience that, although cases obtained in less than ten hours may be satisfactory for certain purposes, the hardness as measured by the microcharacter has always been very much less than the hardness resulting from a long-time treatment.

The authors agree with Dr. Homerberg that there is still much work to be done and hope to continue their studies.

Regarding Dr. Sawyer's discussion. We were very pleased to receive his comments and agree with him that the work here described not only has very real practical significance, but also gives a new line of attack on the theoretical phase of the problem and helps to clear up some of the difficulties in explaining the mechanism involved.

Mr. McQuaid's remarks are very much to the point. As he indicates, the economies involved will have to be determined by actual plant scale operation. Regarding the low temperature of operation, our opinion has been confirmed by further tests at high temperatures. Increasing the temperature increases the depth of case but decreases the hardness. It may well be that for many applications, however, the decreased hardness would be sufficient, so that a higher temperature would be advisable.

A FEW PRACTICAL FUNDAMENTALS OF THE NITRIDING PROCESS

By H. W. McQuaid and W. J. Ketcham

Abstract

This paper gives the results obtained in attempting to determine the effects of some of the factors of the nitriding process on the depth-hardness curves as shown by the Vickers test. The results shown indicate that heat treatment prior to nitriding is essential in order to obtain satisfactory toughness and resistance to shock load. The results shown indicate that decarburization is not necessarily detrimental to the nitriding operation, and on the other hand they indicate that the lower carbon content results in increased hardness. Curves are shown which indicate that a certain percentage of undissociated ammonia must be maintained and it is believed that circulation is necessary to prevent the accumulation of hydrogen on the surfaces to be nitrided. The tests made do not show apparently beneficial effects from the use of a fan, but this is believed to be due to special conditions existing in the test, as commercial results indicate the need of circulation for the best results. Tests made with tantalum to eliminate or reduce the hydrogen on the surface being nitrided indicate that the hardness is decreased thereby. Increase in pressure is shown to result in increased depth of penetration of the hardness, but with a reduction in the maximum. Apparently increasing the pressure has similar effects on the depth-hardness curve to increasing the temperature.

An Attempt to Arrive at the General Effects of the Variables of Pressure, Circulation, and Dissociation in the Nitriding Process

DURING the past year, while there has been a great interest in the production of nitrided parts and a large amount of research work by the interested producers of nitriding steels and users of nitrided parts, there has been, up to this time (June), very little

The authors, members of the society, are connected with the Timken-Detroit Axle Co., Detroit. H. W McQuaid is metallurgist and W. J. Ketcham assistant metallurgist of this company. Manuscript received June 15, 1929.

published data which would indicate that there have been any remarkable developments in the process.

It is customary at the present time to use a steel containing principally aluminum, chromium, and molybdenum as the characterizing elements, and to treat parts made from this steel in an atmosphere of ammonia at 1000 degrees Fahr. Thus, the common method is to follow out the original specifications as given by Dr. Adolph Fry. The use of a furnace having a circulating atmosphere has been found to be advantageous and the necessary time of nitriding using such a furnace has been found to be not more than about 24 hours, for most work. The use of benzine and similar compounds in combination while seemingly of value is not commercially used to any extent as far as is known.

Where the nitriding process has been properly carried out and sufficient care has been taken to eliminate variables introduced by neglecting some of the important controlling factors, the results have been satisfactory. It is safe to say that parts which have been properly nitrided from the special nitriding steels are in practically every way superior to a corresponding case hardened piece. The resistance of the nitrided surface to abrasive wear has been proven to be from five to seven times better than the best carbon or alloy case hardened steel. This has even been found to be true where ordinary carbon steels have been given a superficial hardness by nitriding and operating against a case hardened alloy steel surface which showed a scleroscope hardness of more than 80. The fact that the hardness of the nitrided part can be obtained without commercial distortion is of the greatest advantage in many parts. Inasmuch as most case hardened parts are subsequently ground to obtain a desired size, it is evident that no small saving can be made in the grinding time on many parts by nitriding. It has also been found that the hardness obtained by nitriding is retained at working temperatures as high as 1200 degrees Fahr. and that pieces which are nitrided are practically as resistant to atmospheric corrosion as parts made from the ordinary stainless steel.

Thus we have in the nitrided piece, an article which is extremely hard and wear resistant, and at the same time capable of retaining this hardness at high temperatures, and in combination with these properties, the valuable property of being unaffected by most atmospheric corrosive influences, and commercially free from distortion. With these advantages, it would seem that nitriding would soon develop into

a competitive position with the case hardening steel, and in fact supercede the case hardened part for most uses. The process, if carried out on the same scale as is usual with case hardening parts, should be no more costly, so that we must look for the factors which tend to retard the adoption of nitriding steels, either in the cost of the materials or in some disadvantages connected with the processing. One of the disadvantages of the nitriding steels is the difficulty in machining. Most case hardening steels, being low in carbon, are relatively soft and easy to machine. The nitriding steels with their higher carbon content, in combination with the alloys which they contain, are more difficult to machine, although it is possible that this disadvantage may be overcome by some variation in the analysis or in the treatment. At the present time, difficulty in machining constitutes one of the primary disadvantages of the nitriding steels. It is also difficult to protect parts which are to be nitrided, but this will no doubt be overcome commercially with the more extended use of the nitriding steels. At the present time, nickel plating seems to offer the best medium for inhibiting nitriding, and presents no great difficulty in its use.

Another important factor retarding the more extended use of the nitriding steels is their first cost. It is generally found that the introduction of a material which has a very tangible disadvantage in higher first cost is difficult to achieve in spite of more intangible savings to be obtained in processing. For this reason, it is extremely difficult to change from a low priced carburizing steel to a higher priced nitriding steel, until all the savings in processing are firmly established. There will always be special applications where the advantages in processing are so obvious that the first cost is of little moment, and it is to these applications that the nitriding steels to date have generally been applied. The general adoption of these steels will, without doubt, be slow at the present price, but it is believed that each reduction in price will see a wider application and that the field of the nitriding steels will be to a considerable extent dependent upon the price.

Although intensive research has been and is being conducted into the nitriding process, the exact mechanism of the nitriding phenomenon is not understood. From a strictly commercial standpoint, the user of the nitriding process is interested in reducing the time of the operation, eliminating variables which are difficult to control, and the development of a steel for nitriding which is easy to machine, and low in first cost. The user is also interested in several minor details

such as the protection of surfaces which are to be left soft, and the reduction in the amount of ammonia necessary. In determining the fundamentals involved in nitriding, and their effect upon the commercial results, a large amount of work will be necessary in order to determine the best combination of temperature, time, pressures, and analysis. Combinations of two temperatures seem to have advantages. Combinations of pressures and the use of different pressures than now advocated are factors which must be determined. The effect and function of the aluminum in the steel, and the hydrogen in the process should be carefully investigated, and the effect of heat treatment, etc., of the part to be nitrided must not be overlooked.

At the Timken-Detroit Axle Co. considerable nitriding research work is being conducted with a view to reducing the maximum time necessary to at least 24 hours, and to obtain a case which is not only hard, wear resistant, etc., but which can be made to stand up under heavy shock loads, and in every way possible be equal to case hardened alloy steels for such parts as ring gears and pinions. At the same time an effort is being made to develop a steel which will have machining properties and a first cost which will make it competitive with the alloy case hardening steels.

It is generally advisable in developing new processes and materials to determine the basic fundamentals upon which the process is founded, and it will, no doubt, prove that a thorough understanding of the part which the aluminum and hydrogen plays in the nitriding process would be of the greatest value in building up the commercial application of the process itself.

The work which Dr. Fry has done, as shown by his published results, indicates that there is considerable doubt as to the real reason for the hardness of the piece after subjecting it to the nitriding process. Dr. Fry has not made clear just why steels with aluminum should react as they do nor is it clear as to how the hardening effect is obtained.

The object of this paper is to pick out from the mass of data which is being accumulated at the Timken-Detroit Axle Co., some pertinent facts of value to those interested in the nitriding process. The data presented is, to the best of our knowledge, indicative of the results which should be obtained in practice, but it is not safe to say that some factor has not been overlooked which may have a more impotrant bearing on the results than those presented. It is the intention of the authors, as new information is obtained, to present it

for the criticism of the interested nitrider, and it is hoped that the present paper will be looked upon as a more or less tentative progress report, with probably more important information to be presented at a later date.

Except as noted, the steel which is used as standard for making tests at the Timken-Detroit Axle Co. is the chromium-aluminum-molybdenum steel manufactured by one of the leading alloy steel makers, and analyzes approximately as follows:

	Per Cent
Carbon	0.36
Manganese	0.51
Chromium	1.49
Aluminum	1.23
Molybdenum	0.18
Nickel	0.50
Silicon	0.27
Phosphorus	0.013
Sulphur	0.010

This steel as received from the maker is apparently in the heat treated condition, although it is advisable before nitriding to heat treat every piece, unless brittleness is no disadvantage.

If the nitriding steel is in a pearlitic condition before nitriding, it is impossible to obtain a finished piece which is not extremely brittle. On the other hand, if care is taken in the heat treatment to insure a sorbitic condition, the resulting nitriding piece is much tougher than the corresponding carburizing piece. This toughness seems to be a characteristic of the core and not of the case. Properly nitrided, it should be possible after the case is cracked to bend the nitrided piece to a considerable angle. In order to demonstrate the effect of heat treatment on toughness, pieces from the same bar were made into standard Izod impact test pieces and nitrided together. The results obtained were as shown in Table I.

Table I

Izod Impact Test Results of Samples Nitrided 24 hours at 1000 Degrees Fahr.

Treatment	Notched Values Ft.-Lbs.	Unnotched Values Ft.-Lbs.	Fracture
None	½ to 1	1 to 1½	Crystalline Coarse
1600°F oil quench	33 to 38	88 to 89	Fibrous
1700° F oil quench	38 to 43	97	Fibrous
1800° F oil quench	43 to 46	116	Fibrous

These results indicate quite conclusively the value of quenching before nitriding. It is quite necessary that the quenching temperature

be at least 1600 degrees Fahr. and on heavier work a quenching temperature of 1700 to 1750 degrees Fahr. is suggested. Pieces quenched at 1500 to 1550 degrees Fahr. were little if any better than the unquenched pieces. It is possible that the nitriding steels are more sluggish than usual and a much longer time at 1500 degrees Fahr. would have produced satisfactory impact. Where the steel is to be worked before nitriding as is usually the case, and where distortion in nitriding must be a minimum, the steel must be tempered after quenching. This tempering treatment is generally above the nitriding temperature and for the easiest machining is generally approximately 1300 degrees Fahr.

Experiment No. 1

Effect of Carbon on the Depth-Hardness Curve

An experiment was made to determine the effect of the carbon content on the nitriding results. This was done by subjecting a round bar of molybdenum-aluminum nitriding steel to an oxidizing atmosphere so that a decarburized layer of approximately $\frac{1}{16}$ of an inch was obtained. This bar was then machined to a square with the original surface at the corners as shown in Fig. 3. Samples from this bar were then nitrided for 24 hours at 1200 degrees Fahr., and the results checked by means of the Vickers hardness tester and the microscope. Fig. 1 shows the microsection of the nitrided case at the decarburized portion of the bar. Fig. 2 shows the nitrided case along the undecarburized portion of the bar close to the section of Fig. 1. An analysis was made of the decarburized portion which showed a carbon content of 0.02 per cent. The Vickers readings as shown in Fig. 4 indicate that the penetration of the hardness was deeper and just as high on the low carbon section as on the high carbon section. Transverse Vickers readings taken at the same depth of case show a drop of approximately sixty points in Brinell reading from the decarburized to the original material.

No particular conclusion is drawn from the above experiment, except to say that it indicates that the nitriding action does not seem to be adversely influenced by the carbon content. If any conclusion is drawn it would be that a low carbon content nitrides more readily than a high carbon piece which is exactly contrary to published directions for nitriding. The presence of needles is very marked in the

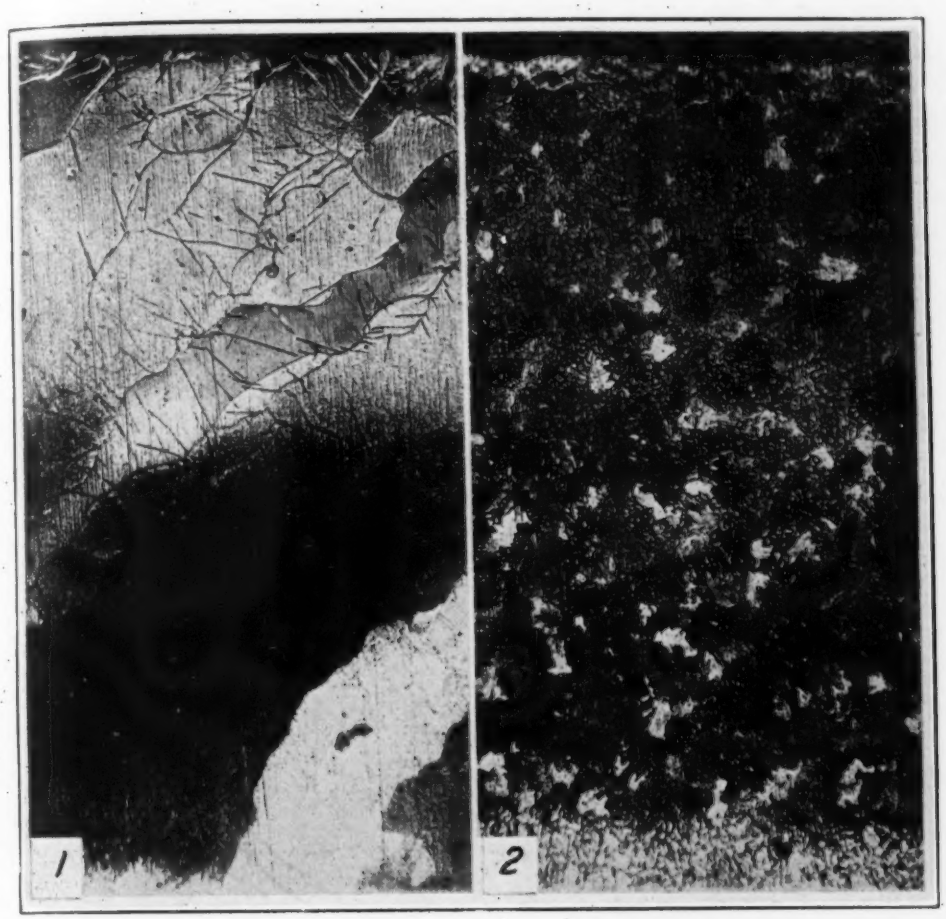

Fig. 1—Photomicrograph of Nitrided Case Through Decarburized Zone. Nitric Acid Etch. Carbon 0.02 Per Cent. × 100.
Fig. 2—Photomicrograph of Nitrided Case Through Undecarburized Zone. Nitric Acid Etch. Carbon 0.27 Per Cent. × 100.

low carbon zone, and apparently absent in the higher carbon zone. Apparently these needles are much more prominent in the larger grains of the lower carbon steel. They have, however, been detected in the finer grains of the higher carbon portion of the piece at a much higher magnification, but do not seem to be so numerous as in the lower carbon grains, nor are they found so far below the surface. The fact that the carbon does not seem to have a definite quantitative relation to the nitride effect would indicate that the nitrides are not formed from the decomposition of the carbides as was once believed by the writer. The penetration of the nitriding action is undoubtedly more rapid in the lower carbon material, and it would seem from this that a lower carbon nitriding steel would be more effective. On the

other hand, the nitrides seem to build up a coarser network in the low carbon area, and it is probable that a lower carbon nitriding steel would be more brittle when nitrided at the higher temperature. This offers what might be an important line of research, since the low carbon steels are undoubtedly easier to machine.

Experiment No. 2

The Effect of Ammonia Flow and Dissociation on the Depth-Hardness Curve

This was an experiment in which the attempt was made to determine the general effect of the ammonia flow and dissociation by comparing work nitrided at the same time, temperature and pressure,

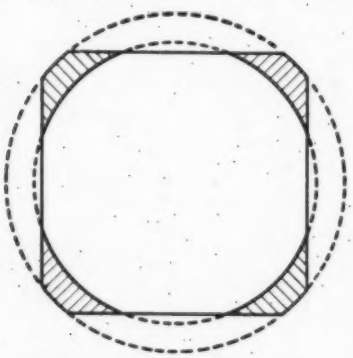

Fig. 3—Diagram Showing How Decarburized Zone was Obtained. Dotted Lines Indicate Original Bar and Depth of Decarburization. Full Lines Indicate Cross-Section of Test Piece for Nitriding.

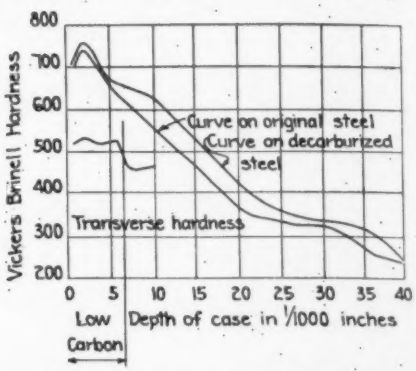

Fig. 4—Curves Showing Depth-Hardness Curves on Decarburized and Undecarburized Nitrided Surfaces—Also Transverse Curve Showing Drop in Hardness with Increase in Carbon.

but with different concentrations of ammonia. Tests were run at 1000 degrees Fahr. for 10 hours in approximately one inch of water pressure under three rates of flow of ammonia. In one case the ammonia was passed through the retort continuously at such a rate that the dissociation was approximately 88 per cent during the entire 10 hours. In the second case the ammonia was maintained at the same rate of flow and dissociation as in the first case for 30 minutes, after which time it was shut off and the retort maintained in a gas-tight condition at heat for a total time of 10 hours. In the third case the ammonia was passed through the retort and then shut off while the retort was still cold. The closed retort was then brought to heat and maintained at 1000 degrees Fahr. for 10 hours; the pressure being approximately one inch of water during this period.

Fig. 5 shows comparative depth-hardness curves of samples taken from each run. Although there was still a considerable percentage of ammonia in the retort after each run, the curves indicate that for a given time and temperature, the depth-hardness of the nitrided case depends upon the amount of undissociated ammonia above a certain minimum. It would probably be better stated to say that above a certain percentage of hydrogen the formation of nitrides is difficult

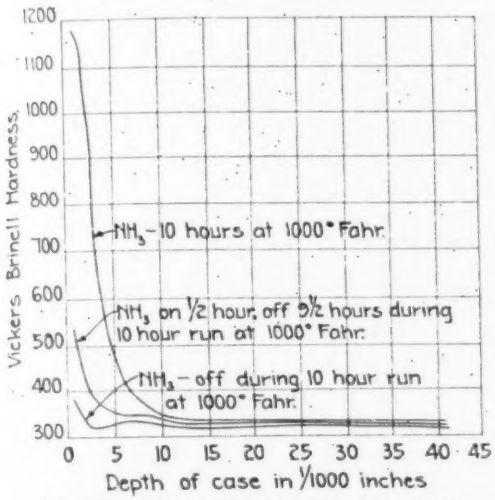

Fig. 5—Curves Showing Results of Ammonia Concentration.

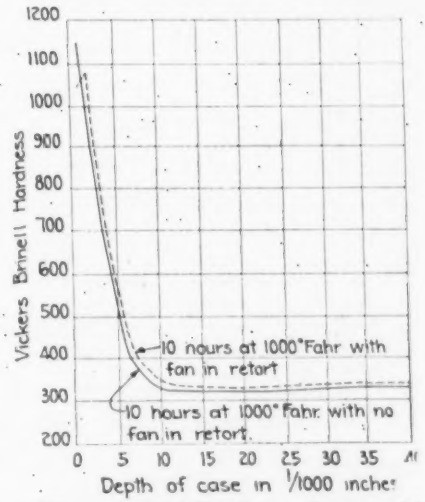

Fig. 6—Depth-Hardness Curve with and without Fan Circulation.

and if the percentage of the dissociation products is too great, nitriding ceases. This agrees with the statement of G. S. Newth[1] that metallic nitrides can be formed at temperatures between 400 and 800 degrees Fahr. in a stream of ammonia, but that they can only be produced in the presence of a large excess of ammonia gas because of the fact that the metallic nitrides are decomposed by hydrogen. Applying these results in a commercial way, it is evident that either a too high dissociation rate or too slow a circulation rate will have an adverse influence on the nitriding. If the dissociation is too high, the percentage of hydrogen may be sufficient to inhibit the nitriding action and if the circulation rate is too low the concentration of hydrogen at the surface to be nitrided may be sufficient to prevent the formation of nitrides.

Experiment No. 3

Effect of Circulation on Depth-Hardness Curve

In this experiment an attempt was made to determine the effect

[1]G. S. Newth, "Textbook of Inorganic Chemistry," Longmans, Green & Co., 1902.

of circulation on the depth-hardness curve where the dissociation rate was as nearly constant as possible. In one experiment a small fan was fitted in the end of the experimental retort and tests were run; some with this fan in operation and others with the fan at rest. The attempt was made to maintain a uniform dissociation in each test, and it can be stated for purposes of comparison that the variation did not exceed plus or minus 5 per cent. The results of these exper-

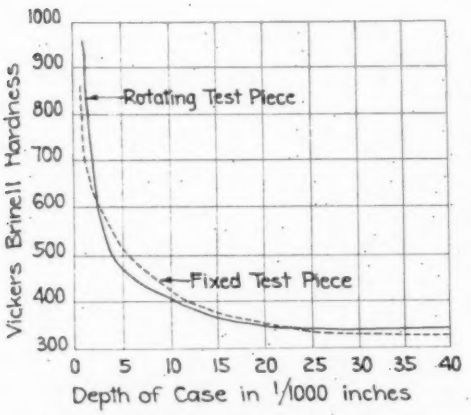

Fig. 7—Showing Depth-Hardness Curves from Fixed and Rotating Test Pieces in Ammonia at 1000 Degrees Fahr. for 10 Hours.

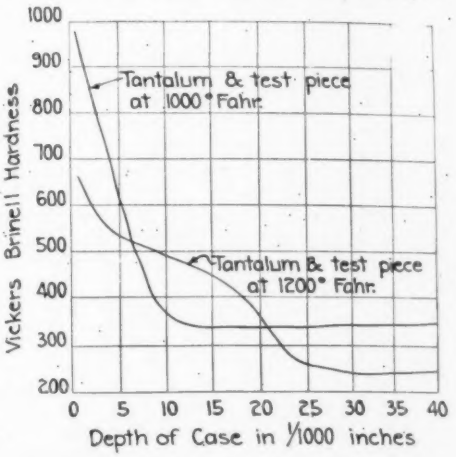

Fig. 8—Showing Effect of Tantalum on Depth-Hardness Curve. Ammonia—10 Hours at Temperatures Shown.

iments are shown in Fig. 6. Other experiments were run in which the retort was so arranged that some of the test pieces could be rotated at a high speed, while the remainder were fixed. In this experiment test pieces were clamped to a rotating bar which caused them to revolve at approximately 3100 revolutions per minute while in the same tube samples were placed which were fixed in position. Fig. 7 shows the depth-hardness curves of the rotating and fixed samples. A study of the curves in Figs. 6 and 7 will show that practically no difference was obtained between the fixed and rotating samples or with or without the fan circulation. This does not necessarily imply that circulation is unadvisable, but in the writer's opinion indicates that the natural flow of the ammonia was probably sufficient to prevent any tendency for the hydrogen to concentrate about the test piece.

Experiment No. 4

An Attempt to Decrease the Hydrogen Effect

In this experiment test pieces were covered with tantalum scrap

and runs were made at 1000 degrees Fahr. for 10 hours and at 1200 degrees Fahr. for 10 hours. The object of this experiment was to attempt to decrease or remove the influence of the hydrogen and it was thought that the results would be an improvement in the depth-hardness curve. The results indicate, as shown in Fig. 8, that the tantalum addition resulted in no improvement, and in fact the indications are that if the removal of the hydrogen was effected by the tantalum, that this is not an advantageous removal. The samples which were treated with tantalum had a distinct color, being a silvery white and free from any indication of oxides or other discoloration. This is a line of research which would be profitable if extended. Tantalum has the power to absorb large amounts of hydrogen as well as nitrogen. It is understood, however, from the published data available that it will absorb hydrogen to a much greater degree, which should have resulted in an increase of nitrogen at the surface of the work.

Experiment No. 5

The Depth-Hardness Curve Obtained with a Combination of Low and High Temperature Nitriding

Runs were made in which the temperature was held at 1000 degrees Fahr. for five hours and then raised to 1200 degrees Fahr. for the second five hours, and the work then cooled slowly. This was done in order to check results which indicated that the use of the two temperatures would result in a considerable increase in depth without sacrifice of hardness, as shown by the depth-hardness curves. It has been the previous practice of the writer to recommend for some work where extreme hardness is not the criterion, to nitride at two temperatures, i. e., 1200 degrees Fahr. for 10 hours, followed by 975 degrees Fahr. for 15 hours. In commerical runs this has given very satisfactory results and in several cases exceptionally good results. It was thought that there may have been some effect which prevented the building up of the nitrides on the surface, and thereby resulting in a softer surface at 1200 degrees Fahr. so that a second period at a lower temperature would build up the higher nitride and give not only a deeper penetration, but a very much harder surface. For some reason it has been difficult to obtain consistent results in practice, although the best short-time nitriding results which the writer has seen so far have been obtained by this method. It was

thought that the variation may have been due to the different rates of heating up, which resulted in different times at the lower nitriding temperature in moving to 1200 degrees Fahr. It was thought that the time at the lower nitriding temperatures (900 to 1000 degrees Fahr.) resulted in the formation of an initial hard nitride surface

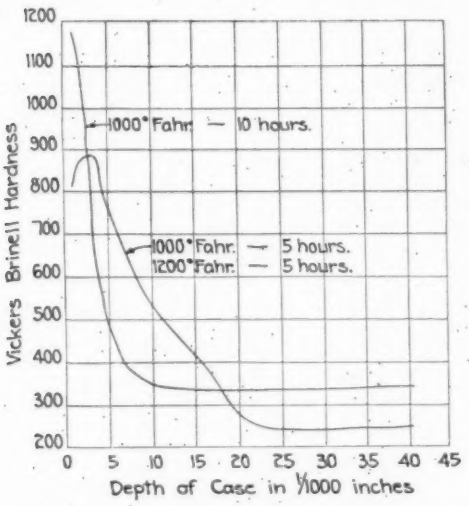

Fig. 9—Variation in Depth-Hardness Obtained by Temperature Variation.

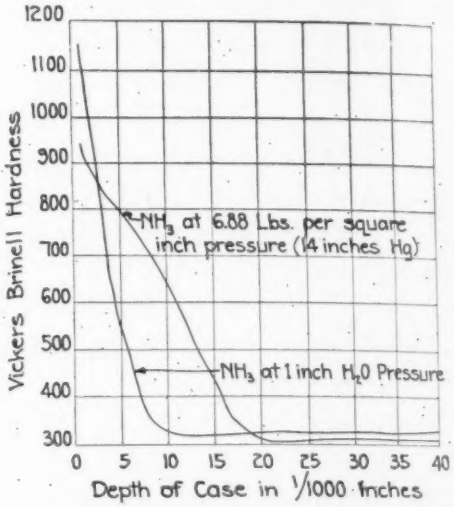

Fig. 10—Depth-Hardness Curve Showing Effect of Increased Pressures. Ammonia at 1000 Degrees Fahr. for 10 Hours.

which increased the hardness and toughness as compared to the surface obtained if a 1200-degree Fahr. temperature was rapidly attained.

The curves shown in Fig. 9 show the depth-hardness curve obtained by nitriding at 1000 degrees Fahr. for five hours and raising the temperature to 1200 degrees Fahr. for a second five hours. It will be noted that this shows a deeper penetration than the straight low temperature run, but the hardness has been materially reduced, indicating that the benefits of the preliminary low temperature run, as far as increasing the hardness of the case is concerned, are lost.

Experiment No. 6

Effect of Pressure on Depth-Hardness Curve

In this experiment, maintaining approximately the same dissociation, tests were run with pressures of 14 inches of mercury and also with one inch of water. The results in Fig. 10 show that the depth is considerably increased by the increase in pressure, but that

the hardness is not so great. The action seemed to be similar to that obtained with the higher temperature run. The pressure experiments indicate that there is apparently something to be gained by increasing the pressure as found by R. H. Hobrock[2] in his paper presented at last year's annual meeting. It is believed that this work could be extended profitably, and it is the intention of the writer to work to some extent along this line of research.

Conclusion

In conclusion it may be stated that in submitting this paper the writers have purposely refrained from introducing any theoretical speculation, although the temptation to do so has been very great. Our experience with nitriding has indicated the excellence of the properly nitrided piece, and also the relatively limited knowledge which seems to be available as to the actual mechanism of nitriding. It is hoped that something may be found in the above which may prove of value and the writers gladly welcome any criticism, either constructive or destructive, in order that no false premises may be set forth to mislead workers in the nitriding art.

Acknowledgement must be made of the help of O. W. McMullan of the Timken-Detroit Axle Co. in making the necessary Vickers tests, upon which this paper is based.

DISCUSSION

Written Discussion: By G. M. Eaton, Molybdenum Corp. of America, Pittsburgh.

The authors have followed a very important line of thought in preparing this paper.

It is essential to learn as much as possible of the basic fundamentals of the mechanics or physical chemistry or metallurgy of the nitriding process, and a large amount of research is under way along these lines. But the immediate need of the men who are producing nitrided parts on a commercial basis is practical knowledge of the process along the two usual lines. First what to do, and second what to avoid.

In our work we have found that one of the possible variables of the process which gives a lot of trouble when not properly controlled is the tightness of the cover joint of the retort. Leakage at this joint is responsible for wide variations in the characteristics of the case.

In connection with the saving of time and cost through the elimination of grinding of the nitrided product, as compared with case carburized

[2]R. H. Hobrock, "Surface Hardening Special Steels with Ammonia Gas," Transactions, American Society for Steel Treating, Vol. 15, April, 1929, p. 543.

parts, there is a gain which we suspect is not fully appreciated. We refer to the ever present possibility of grinding cracks. We have traced down to grinding cracks a surprising number of puzzling failures of ground parts produced in different industries.

These failures have usually occurred as epidemics, which selected embarrassing periods in a most perverse way. The nitrided product is in general immune to this class of trouble.

We expect others who have done more than we in selective nitriding will describe the process of tin plating for inhibiting the nitriding action where desired, and we only mention it to be sure that attention is called to this attractive method.

The report of the authors on the successful nitriding of decarburized surfaces is to us the most surprising feature of the paper.

We wish to ask whether the procedure followed in decarburizing the samples surely produced a condition in the decarburized region, which is an exact replica of the conditions produced in a commerical mill.

On all the steels with which we have worked, we have produced no satisfactory case on decarburized material and it would be a great satisfaction to us to be able to reverse the stand we have taken that mill decarburized material must be removed from surfaces where a sound nitrided case is required.

We will look forward with anticipation to the further progress reports contemplated by the authors.

Written Discussion: By Dr. J. T. Norton, Jr., Ludlum Steel Co., Watervliet, N. Y.

This paper of Messrs. McQuaid and Ketcham brings up points of great interest and importance to users of the nitriding process. The desirability of heat treating nitriding steels is now generally acknowledged, but there is still a large amount of steel used in the annealed condition because of the refusal of many customers to undertake any heat treatment whatsoever and the demand for machinability approximating screw cutting stock.

The effect of carbon on the nitriding operation, as brought out by the authors, in the main, bears out our experience that carbon in itself has no effect on the depth of case and it is probable that a very low carbon will nitride more readily than a medium or high carbon steel. The use of very low carbon nitriding steels has been successful in certain cases, but steel of this character has to be handled with considerably greater care than the higher carbon material, possibly on account of its liability to grain growth. We have recently observed in the case of a nitriding steel of special analysis a total penetration of nitrogen of .08 inches as shown by the copper sulphate etch about twice the normal depth of penetration. This steel contained only .08 carbon and had been annealed at 1450 degrees for ten hours to bring the Brinell down as low as possible. There was considerable grain growth on the outside of the bar and the case was extremely brittle and non-adherent. An unannealed sample of the same steel showed greater depth of penetration than normal with higher carbon

material, but the case was both hard and adherent to the core. Our experience with nitriding decarburized steel has invariably been unfortunate. The case is always extremely brittle and shows no cohesion to the core; often it will fall off of its own accord when the part is moved, and will come off in large flakes when struck even the lightest blow. This condition is probably due to intergranular weakness caused by loss of carbon and consequent penetration of hydrogen and nitrogen into the grain boundaries.

The experimental work done by the authors on the effect of rate of ammonia flow and dissociation is useful and instructive. We have always found it advisable to keep a large excess of ammonia flowing through the system. We have not been able to find any advantage in passing the ammonia over benzol before entering the container or in the use of a catalyzer inside the box. However, to reach any definite conclusion on this subject, a large amount of research work should be carried out.

Written Discussion: By Robert Sergeson, Central Alloy Steel Corp., Canton, Ohio.

The authors are to be commended for their clearness in presentation and for the valuable data and suggestions given.

In the forepart of this paper the trend of aluminum-chromium steels is well discussed. However, there are some points which it is believed should be modified.

One is in regard to protection of parts. The paper states that nickel plating offers the best medium for protection. While this is undoubtedly true, it should also be kept in mind that tinning also offers complete protection. For tinning, parts desired to be protected should be thoroughly cleaned, then washed with cut acid (hydrochloric acid into which zinc is added till there is but little action) and parts either dipped into or have poured on to them the metal solder containing the tin. It is general to use 50 per cent tin and 50 per cent lead. The tin content may be as low as 25 per cent. The protection given by nickel and by tin is shown in photomicrographs, in Figs. 1 and 2 of this discussion.

A second is the cost. It is believed that the cost has been materially lowered since the writing of the authors' paper.

In Experiment No. 1 the authors have suggested that the lower carbon content does not adversely affect the nitriding qualities. The following experiments are well in accord with this statement. Specimens of nitriding steel "G" approximately ½ inch square by $\frac{1}{16}$ inch thick were completely decarburized by annealing in a stream of hydrogen, 8 hours at 1700 degrees Fahr. These decarburized sections were then nitrided 48 hours at 975 degrees Fahr. and found to nitride file hard. A Vickers reading of 850 was obtained on the surface with difficulty owing to the high degree of brittleness. Fig. 3 shows the structure of the nitrided case while Fig. 4 shows the high concentration of nitride needles at the corner of the specimen. The brittleness appears to be due to the nitride network surrounding the individual grains. Longer nitriding cycles on these de-

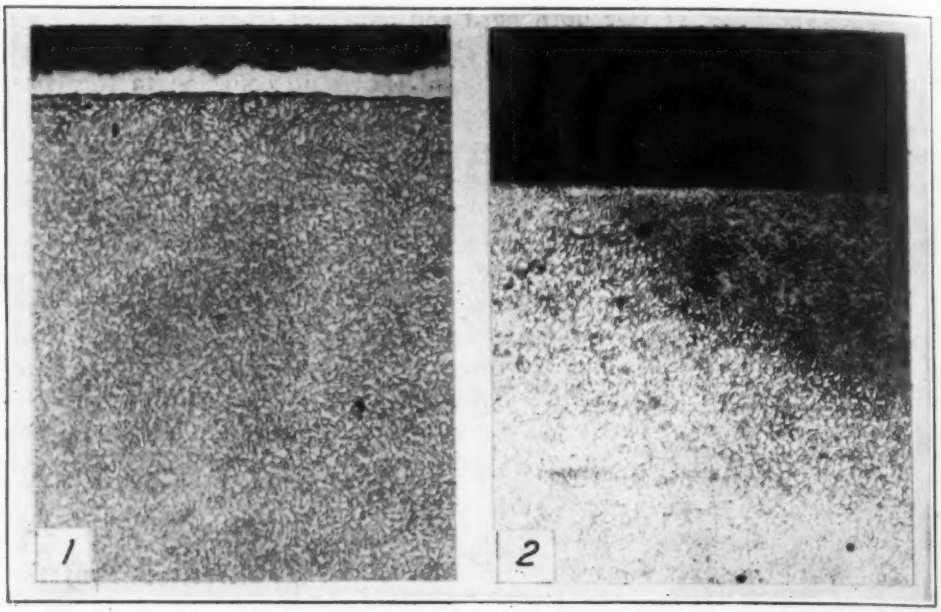

Fig. 1—Showing (white) Nickel Plating on Surface has Prevented Nitrogen Adsorption.

Fig. 2—Showing Junction of Tinned and Original Surface. Dark Area is the Nitrided Area. Nital Etch. × 100.

carburized materials has caused the metal to break up into its individual grains.

If the carbon in steel "G" is spheroidized and specimen then nitrided, excellent hardness is obtained without alteration of the spheroidized structure. Figs. 5 and 6 show structure before and after nitriding respectively, indicating the inertness of the carbide islands.

Again a low carbon nitriding steel analysis, carbon being 0.13 per cent, was nitrided for 90 hours at 975 degrees Fahr. and found to show excellent surface hardness and good penetration. Fig. 7 of this discussion shows the hardness and penetration obtained.

While the above experiments tend to show that carbon is not essential for nitriding, it has also been observed that the toughest nitrided cases are obtained when nitriding a sorbitic structure where carbon is well dispersed so that the form in which the carbon is present is quite important in many cases.

Experiment No. 1. Fig. 5 of the paper points out very interesting results. It shows that a certain amount of flow is essential. As to the cause of the low hardness and lack of penetration obtained in the two lower curves (Fig. 5), it is believed that the lack of nascent nitrogen and the presence of molecular hydrogen are responsible. Nascent nitrogen is responsible for nitriding for molecular nitrogen gas will not nitride. Also if a nitrided specimen 1000 Vickers Brinell is annealed in molecular hydrogen at 1050 degrees Fahr. its hardness will fall to 500 Vickers Brinell in 10 hours. At least this is the result of a test. It would be interesting to note the effect

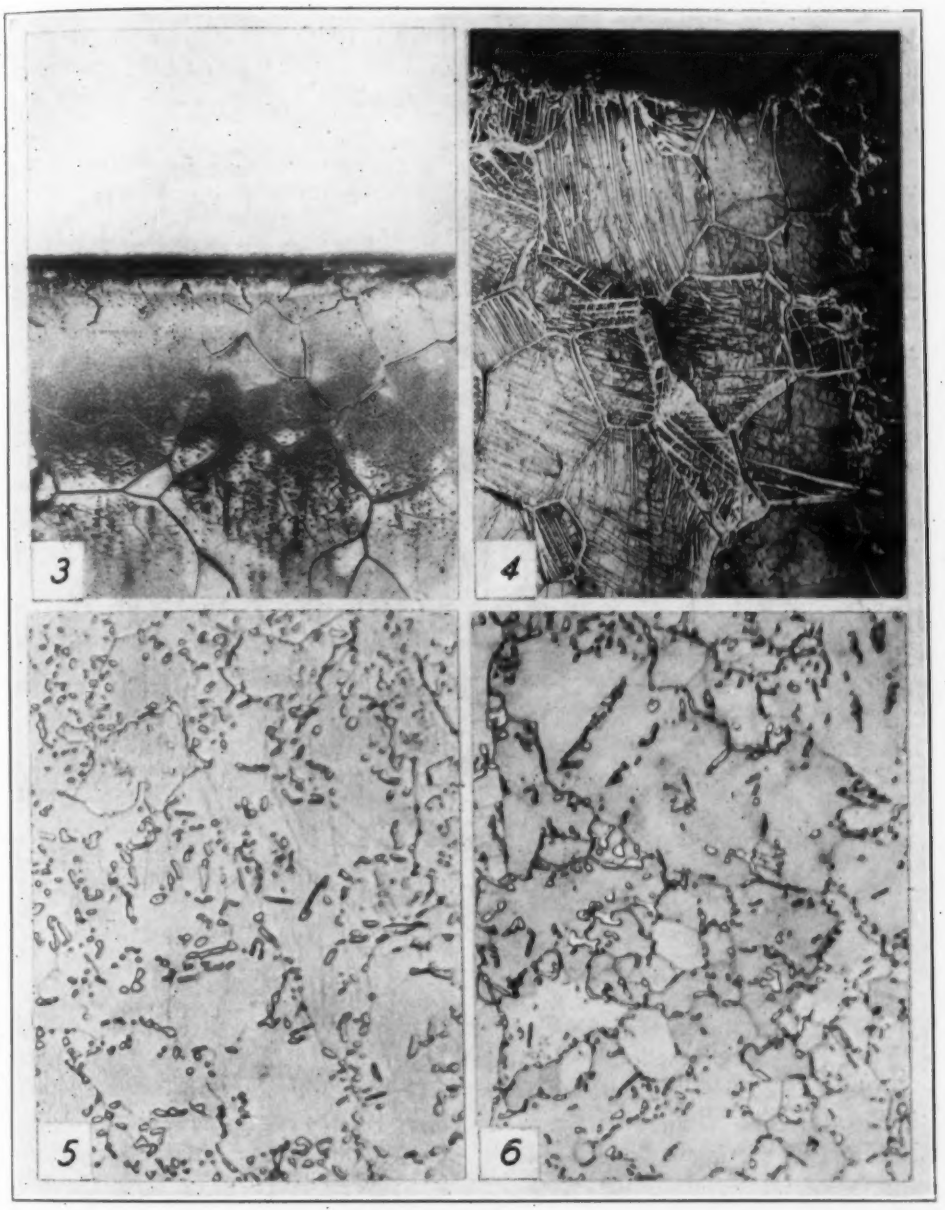

Fig. 3—Steel G Decarburized in Hydrogen and Nitrided 48 Hours at 975 Degrees Fahr.
Fig. 4—Same as Fig. 1 Showing Concentration of Nitride Needles at a Corner. Nital Picric Etch. × 100.
Fig. 5—Steel G Spheroidized. Brinell 156. Nital Etch. × 850.
Fig. 6—Steel G Spheroidized and Nitrided 90 Hours at 975 Degrees Fahr. Vickers Brinell 1000. Nital Picric Etch. × 850.

of longer nitriding cycles under same conditions as shown in Fig. 5 of the paper.

Experiment No. 3. It has been experienced in small laboratory nitriding containers the passage of the ammonia gas produces sufficient circulation

but in larger containers for commercial work a circulating fan is highly desirable to obtain uniformity of nitriding throughout container. A question naturally arises as to what effect has circulation when higher temperatures, 1100 and 1200 degrees Fahr., are used. Have the authors any data regarding this?

Experiment No. 4. Can the authors give the relative absorption power tantalum has for both hydrogen and nitrogen at temperatures 900 to 1200 degrees Fahr.?

Experiment No. 5. In regard to the duplex run, it has been noted that if the low temperature of 950 or 1000 degrees Fahr. is run first and followed

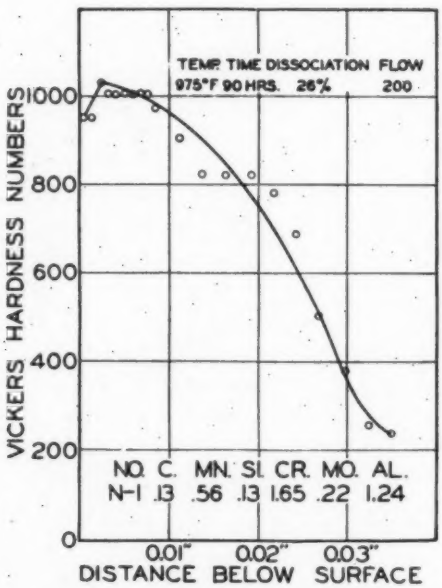

Fig. 7—Hardness Penetration Obtained on Low Carbon Aluminum-Chromium-Molybdenum Steel.

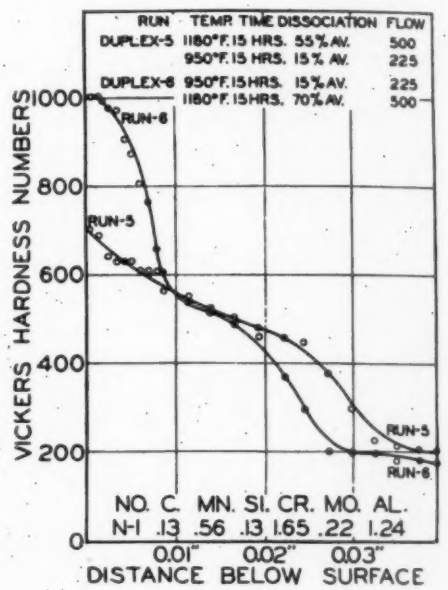

Fig. 8—Duplex Cycle.

by the high temperature, a high surface hardness is obtained equal in fact to that of a single run at the low temperature. The reverse cycle, i.e. nitriding at high temperature followed by a low temperature, however produces a lower hardness on the surface. This is shown clearly in Fig. 8 of this discussion. Compare with Fig. 7 which is a single run on the same steel. It is believed that the 5-hour periods of duplex runs shown in Fig. 9 of paper were too short to produce maximum surface hardness.

Experiment No. 6. The effect of pressure in increasing the depth but lowering the hardness is significant. Have you investigated various rates of flow at the increased pressure?

Oral Discussion

W. J. MERTEN: Mr. McQuaid directs attention to the effect of dissociated hydrogen in the nitriding chamber and I am convinced that it is this element which limits and restricts economically practical nitriding with

ammonia to a very small number of alloy steels. From the behavior of the different alloy steels aluminum seems to inhibit to a large degree the deleterious behavior of hydrogen during nitriding. I believe this is worth investigation and verification.

In our work we certainly do find a definite detrimental effect from the presence of water vapor in the nitriding chamber and our results have been decidedly better and consistently so after a perfect seal composed of wire gasket and liquid lead was introduced. We therefore cannot subscribe to Mr. McQuaid's statement that water vapor present during nitriding does not affect the final results.

Authors' Closure

In replying to Mr. Merten's oral discussion it is observed that according to him his results have been decidedly better, and consistently so if a perfect seal composed of a wire gasket and liquid lead was introduced. It is not my intention to father the idea that a leaky retort would not have a detrimental effect on the nitriding. It does not necessarily follow, however, that a leaky retort involves the presence of water vapor in the ammonia tank, although this is possibly true at low temperatures. The use of special ammonia drying equipment has not been found by us to be necessary although it might be that under the conditions existing in Mr. Merten's equipment, that water vapor might affect the operation.

In reading the written discussion by G. M. Eaton of the Molybdenum Corporation of America, we note his reference to the importance of grinding cracks. We agree fully that grinding cracks have always been one of the most difficult things to contend with in grinding hard surfaces, particularly in such parts as cam shafts, wrist pins, worms, etc. We suspect that if the true effect of grinding cracks on the economic value and service results were fully appreciated, the introduction of nitriding steels would not be very difficult.

We are well aware that tinning provides a satisfactory method of inhibiting the nitriding action and have been using this method ourselves. The nickel plating method offers what is apparently a cheaper practice in commercial production.

We can assure Mr. Eaton that the procedure followed in decarburizing the samples produced a condition which is an exact replica of the conditions produced in a commercial mill, because that was the way in which the decarburized samples were obtained. The decarburized surface was obtained by selecting a hot rolled bar which had been oxidized in the rolling. What we wish to bring out in reporting the results of the investigation of the decarburized surface was to indicate that just as satisfactory, if not a more satisfactory nitrided part could be obtained in the low carbon steel as from the higher carbon. It is my opinion that the brittleness and difficulty associated with the ordinary decarburized surface is entirely due to the coarse grain commonly associated with this condition, and that no trouble would be had if the low carbon or decarburized steel could be properly refined before nitriding. In other

words, in the interest of easier machining, I would recommend that we experiment with the low carbon nitriding steels and develop a heat treatment which will insure a sorbitic structure with consequent absence of brittle surface. In all the investigations of the decarburized surfaces reported by Mr. Sergeson, Mr. Homerberg, etc., this condition was obtained by very prolonged heating in hydrogen or oxygen followed by slow cooling with the result that after the decarburizing action the material was in an annealed condition, which in itself is conducive to poor results particularly when the grain size is excessive, as it usually is following the decarburizing action. Inasmuch as it is necessary to quench the nitriding steel from a rather high temperature, it is possible that the low carbon nitriding steel, say in the vicinity of 0.20 per cent carbon, would be refined by a high quench followed by a proper tempering operation. This is a line of research which should be, by all means, developed by the maker of nitriding steels.

We appreciate the discussion of J. T. Norton, Jr., of the Ludlum Steel Company, and note that his results with decarburization are similar to our own. He notes that an unannealed sample of 0.08 per cent carbon nitriding steel showed a greater depth of penetration than normally with higher carbon steel, and the case was both hard and adherent to the core; whereas with the annealed sample the case was extremely brittle and loosely adherent. We believe that he is correct in his statement that the condition of extreme brittleness and lack of cohesion is principally due to inter-granular weakness caused by loss of carbon and consequent penetration of hydrogen and nitrogen into the grain boundaries.

We certainly appreciate the carefully prepared discussion of Mr. Sergeson of the Central Alloy Steel Corporation, and would again state that we did not wish to infer that the nickel plating was the only method of inhibiting the nitriding action, but as stated in our paper, suggested that nickel plating seemed to offer the best medium for inhibiting nitriding, and presented no great difficulty in its use. The tinning method is, of course, quite satisfactory and for some parts equal to, if not more satisfactory than, the nickel plating.

Since our paper was written, i.e., in June, we understand that the cost of nitriding steel has been materially lowered, but it is still, of course, considerably above the standard grades of alloy carburizing steels. The discussion of the decarburizing action on the nitriding results given above in answer to a discussion by Messrs. Eaton and Norton, will apply equally well to the discussion of Mr. Sergeson on this subject.

It is very interesting to us to note that spheroidized aluminum-chromium steel nitrides well without alteration of the spheroidized structure, indicating, that the nitriding action in itself is not the cause of the brittleness in low carbon steel and carbides as such do not affect the nitriding action to any important degree. In those cases where higher strength of core is required, the lower carbon nitriding steels would, of course, be at a disadvantage, but in most cases it seems that the carbon content should be as low as possible consistent with obtaining commer-

cially a fine grain sorbitic condition before nitriding. In regard to the effect of nascent nitrogen and molecular hydrogen we are convinced that this is a most important line of research and are bending every effort to complete the work we have under way in this field. In regard to Experiment No. 3, we find that with fan circulation at the high temperatures, i.e., at 1200 degrees Fahr., dissociation is so great that it is very difficult to obtain satisfactory results as compared with the retort type of nitriding. We have found that the use of a fan in our standard retort at these temperatures resulted in very poor results, the nitride formed being apparently reduced on the surface so that we had what was apparently pure ferrite in a granular form. By removing this from the surface with a sand blast, we were surprised to find an extremely hard surface underneath indicating that the nitriding action by diffusion produced a satisfactory case, but apparently the hydrogen and molecular nitrogen in excess tended to break down the nitrides at the surface. This, of course, is a line of research which should be well investigated, as it is believed that the time of nitriding could be materially reduced if the dissociation in the type of furnace shown in Fig. 7 of Mr. Sergeson's paper could be held below 40 per cent at 1200 degrees Fahr.

We have no data on the relative absorption power of tantalum of both nitrogen and hydrogen at temperatures from 900 to 1200 degrees Fahr. The only data we have is to the effect that heated tantalum will absorb 742 times its own weight of hydrogen. A rather extensive search of available literature failed to reveal any references as to the absorption power of tantalum for nitrogen.

In regard to the effect of pressure on increasing the depth, we have not been able to investigate with various rates of flow at the increased pressures due to lack of time. We are attempting, at the present time, to control dissociation by means of combinations of higher pressures, and temperatures, expecting to obtain increased hardness and increased depth at the high temperature.

We appreciate very much the interest of those who have discussed our paper, and trust that the combined interest of those who took part in the Nitriding Symposium will result in the rapid development and application of the nitriding process.

USE OF NITRIDED STEEL IN HIGH TEMPERATURE —HIGH PRESSURE STEAM SERVICE

By Vincent T. Malcolm

Abstract

This paper deals with the application of nitrided steels for the trim on valves subjected to high temperature and high pressure steam service. It is pointed out that nitrided steel has the ability to resist stress at high temperature over long periods of time; it is corrosion resistant; has a thermal expansion corresponding closely to carbon steel and possesses resistance to wear and abrasion. Only severe service conditions to which nitrided steels have been subjected are described, no details of methods and tests are given.

PROGRESS in the art of steam station design and operation has been so rapid as to bewilder even the men who have given their whole time and thought to this work. Today's economic conditions are imposing upon us the necessity for efficiency in every phase of industrial activity and not the least important is the economical generation of power. That economy of steam generation may be improved by the use of higher pressures and temperatures may be considered an established fact, but the production of this economy is in no small way dependent upon efficient utilization of materials of construction. The improvements are based namely on increase of pressure and temperature and temperatures are restricted to the limit of materials available for such use.

The engineer engaged in the generation of steam needs a comparatively cheap metal that will have high physical properties not greatly impaired by high temperature service. He needs a metal that is resistant to high temperature gases, and one that will hold its surface under heavy sliding pressure, so as not to suffer from abrasion due to the great velocity and pressure of gases used, and in order for a metal to have this resistance to corrosion i. e., scaling and oxidation, it must be stable at temperatures employed, and be capable of resisting for the economic life of the piece of equipment

The author, Vincent T. Malcolm, a member of the society, is metallurgical engineer, Chapman Valve Manufacturing Company, Indian Orchard, Mass. Manuscript received August 16, 1929.

of which it forms a part. In the construction of valves designed to operate at these high temperatures and pressures it becomes a necessity that the working parts of a valve in contact with each other resist "seizing" or "galling."

The complexity of the problems involved as related to design and operation has in a number of instances not been fully appreciated and the conservative attitude of engineers is reasonable in view of

Fig. 1—Photograph of Monel Metal Valve Gate Showing the Result of the Wire-drawing Action of the Steam.

the very limited amount of information available upon the behavior of metals under high temperature and pressure and particularly on account of the way in which it has been presented and regarded.

Various metals and coatings have been used for the trim of valves in high temperature, high pressure service, but after careful experiment and test most of these have been found to have certain limitations, such as high cost, inability to hold their surface, excessive wear, "sticking" or "seizing," "wire drawing," non-resistance to corrosion or abrasion, "scaling," peeling of plated surfaces, "tearing," or great variation of thermal expansion.

Fig. 1 shows wire drawing and abrasion of a monel metal valve gate, while Fig. 2 shows "sticking" and tearing in a stainless steel gate.

After careful experiment and practical test it was found that a nitrided steel possessed properties of extreme hardness, wear and abrasion resistance, chemical stability under superheated steam, combined with a tough core having high impact value and tensile strength,

together with a coefficient of expansion similar to ordinary steels.

It is the author's intention in presenting this paper simply to set forth certain facts which should be borne in mind when considering the use of metals in high temperature, high pressure service, rather

Fig. 2—Photograph of a Stainless Steel Valve Gate Showing the Results of Sticking.

than to describe methods of tests or to delve into the peculiar characteristics of a number of alloys.

The most important considerations to be given to material of construction for use in the generation of steam may be listed as follows:—

1. Ability to resist stress at temperatures over periods of long duration
2. Chemical stability
3. Thermal expansion
4. Resistance to wear and abrasion.

Very little need be said with regard to strength of metals at elevated temperatures as detailed reports have been previously published. Fig. 3 shows the results of long duration tests on nitrided steels, while Figs. 4 and 5 show the fractures obtained from short time tests.

Chemical Stability

Excellent physical properties at elevated temperatures, however, are not the only criteria to be used in selecting metals for this service. Scaling and oxidation are deciding factors. The real

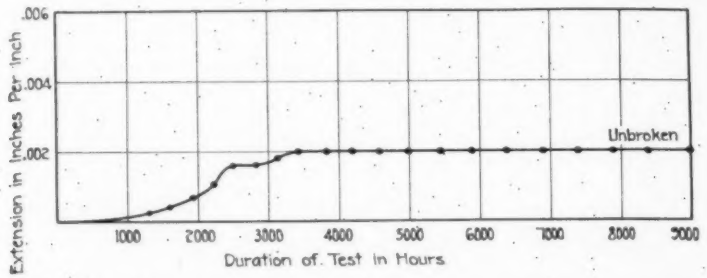

Fig. 3—Curve Showing Results of Long Duration Test on Nitrided Chromium-Aluminum Steel. Constant Temperature 1000 degrees Fahr. Constant Load 10,180 Pounds per Square Inch.

Fig. 4—Tensile Test Bar Showing Character of Rupture of Nitrided Steel.
Fig. 5—Fracture of a Tensile Test Bar of Nitrided Steel.

difficulty in connection with high temperature work is the combining of the necessary physical properties with some particular chemical stability, so as to have a correct design for a complete working unit.

Problems of corrosion at high temperature are far more difficult to solve because of the greater chemical affinity at these temperatures or the disturbing of the chemical equilibrium due to operating conditions.

Nitrided steel resists oxidation and corrosion under the action of superheated steam.

Thermal Expansion

Thermal expansion is one of the most important points that has a direct bearing on the design of valves for safe operation at elevated temperatures and we can reasonably assume that a great many fail-

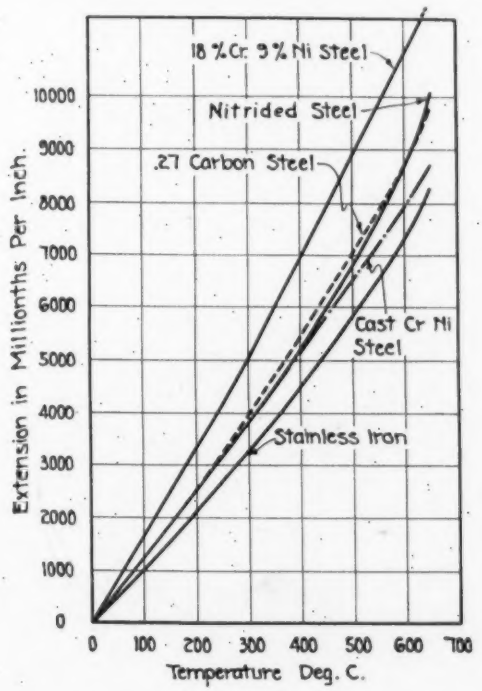

Fig. 6—Curves Showing the Coefficient of Expansion of Several Types of Metals Used in Valve Bodies.

ures of metals at high temperature were caused by the use of a combination of metals that were entirely unsuited for the work or from lack of knowledge on the part of the designer of certain stresses not readily calculated, due to non-uniformity of temperature distribution. It is no easy matter to avoid deformation caused by these temperature stresses if the valve rings are made of metals having an entirely different coefficient of expansion than the valve body and which stresses are probably due to operation at high temperatures.

Fig. 6 shows the coefficient of expansion plotted for several types of metals used in valve bodies and it may be noted that nitrided steel corresponds closely to carbon steel and to its own core.

Wear and Abrasion

Despite the difference in effect observed by different investigators with various test methods, there are a number of general conclusions which may be drawn from studies of wear and erosion, and

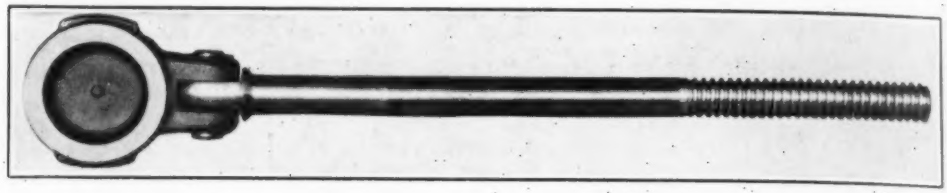

Fig. 7—Nitrided Steel Plug Taken from a Valve after Several Months' Service at High Pressure and High Temperature. This Plug Showed No Wear.

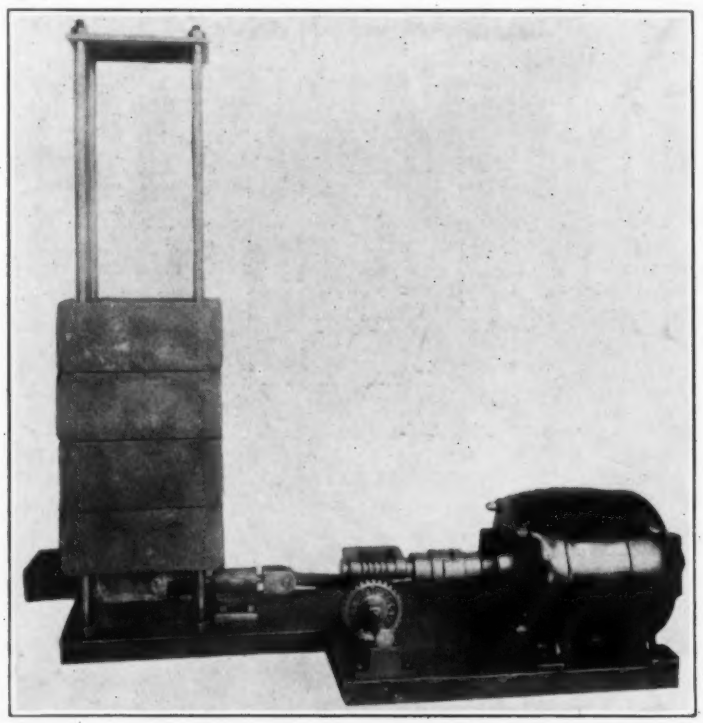

Fig. 8—Wear Testing Machine Designed to Duplicate Service Wear Conditions.

it is probable that more metal articles are ruined or placed out of service by erosion and wear than by any condition other than corrosion, and is due to the ever present tendency for wear to occur when two solid bodies in contact move in reference to each other or by the terrific velocity of the various gases used in high pressure, high temperature work.

Figs. 1 and 2, show results of some of this wear and Fig. 7 is a nitrided steel plug taken from a valve after several months' service at high pressure and temperature, which showed no wear.

The determination in an experimental way as to the ability of metals to resist wear has as yet not been consistant with practical

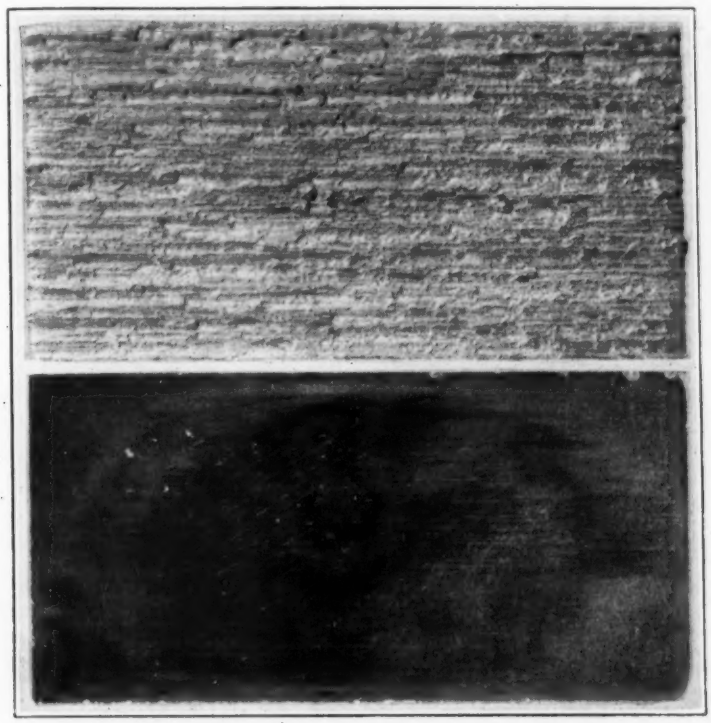

Fig. 9—Specimens of Stainless and Nitrided Steel After Being Tested in the Wear Testing Apparatus. Upper—Stainless Steel. Lower—Nitrided Steel.

experience and each problem must be attacked separately and under like conditions as applied to the service intended.

Fig. 8 shows a wear testing machine designed and built by the Chapman Laboratories to duplicate service wear tests on valves as closely as possible.

Fig. 9 shows specimens of stainless steel and nitrided steel after being subjected to the wear testing apparatus. The stainless steel was subjected to 1000 revolutions at 200 pounds pressure and the nitrided steel to 100,000 revolutions at 200 pounds pressure.

Hardness appreciably improves performance but hardness itself is no certain criterion of the erosion resistance of various metals, and the term "hardness" is at the present time a very indefinite subject

and in order to discuss this subject intelligently it is first necessary to determine, what hardness is. The definition of hardness that will correspond to any physical property is a definition yet to be found, and after a thorough search of the literature with regards to hardness, we believe the best definition to be:—

"By hardness is meant that property of mechanical resistance that is possessed by the outer layer of solid bodies."

Resistance to erosion does not, in general, increase directly with

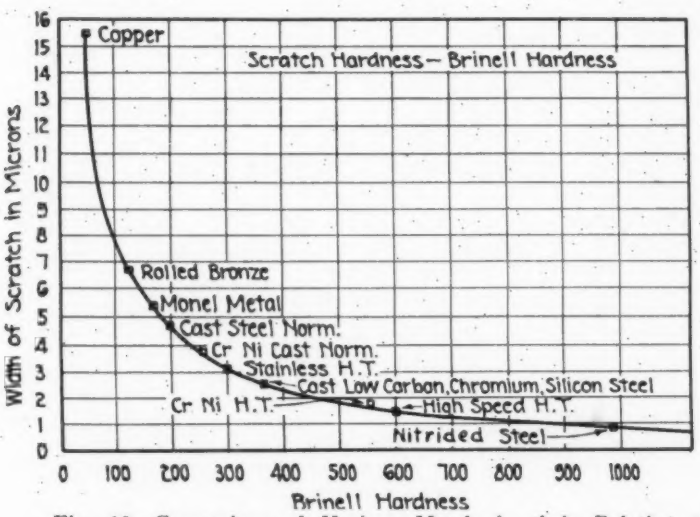
Scratch Hardness– Brinell Hardness
Width of Scratch in Microns
Brinell Hardness
Copper
Rolled Bronze
Monel Metal
Cast Steel Norm.
Cr Ni Cast Norm.
Stainless H.T.
Cast Low Carbon, Chromium, Silicon Steel
Cr Ni H.T.
High Speed H.T.
Nitrided Steel
0 100 200 300 400 500 600 700 800 900 1000
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16

Fig. 10—Comparison of Various Metals in their Relation to Scratch Hardness.

strength or hardness. Both hardness and toughness are important factors in determining the wearing quality of a metal, because hardness increases the resistance to penetration, scratching, and displacement of metal, while toughness makes it difficult to tear off small particles of metal, which particles, when torn off by rubbing or sliding action constitute an abrasive of considerable effectiveness.

Nitrided steel has both hardness and toughness as shown by the following physical properties as used in our valve trim:—

Tensile strength	100,000 pounds per square inch
Yield Point	75,000 pounds per square inch
Elongation in 2 inches..	18 per cent
Reduction of area	35 per cent
Charpy Impact value...	37 foot-pounds.

Fig. 10 shows comparison of hardness between nitrided steel and various other metals.

Properties of Nitrided Case

The properties of our nitrided steels are a case with extreme

hardness and without brittleness, reaching a maximum hardness on the outside surface and extending into the steel for approximately $\frac{1}{32}$ inch. Fig. 11 shows test of valve ring and its lack of brittleness.

Commercial Possibilities

Nitrided steel before nitriding forges and machines readily and no grinding is done after nitriding in order to true up the surface

Fig. 11—Twisting Test of a Nitrided Steel Valve Ring Showing Its Lack of Brittleness.

of valve rings or disks and it must be remembered at this time that certain valves are tested to 5000 pounds hydrostatic pressure without sign of leakage between two nitrided surfaces.

Tests

Tests of nitrided steel as carried out in our plants are fully described in Transactions Vol. XV, January 1929, pages 25 to 30.

Some Actual Working Tests

In order to determine the tightness and durability of the working parts of a valve, there has recently been conducted by one of the large public utility companies a series of tests to determine exactly what happens to a valve when it is closed under full unbalanced pressure for a large number of operations. This report covers a test on a standard 10-inch, 400-pound code valve trimmed with nitrided steel. Fig. 12 shows the method in which the valve was opened in conducting a test. The entire valve was housed in and covered with a loose insulating material so that the valve could be brought up to full temperature. The method of test was as follows:—

After the valve had been set up as shown in Fig. 12, "A" on the inlet and "B" on the discharge were open with "C" and "D" remaining closed. The valve was then steamed for 30 minutes, bringing the temperature to the operating condition. The steam

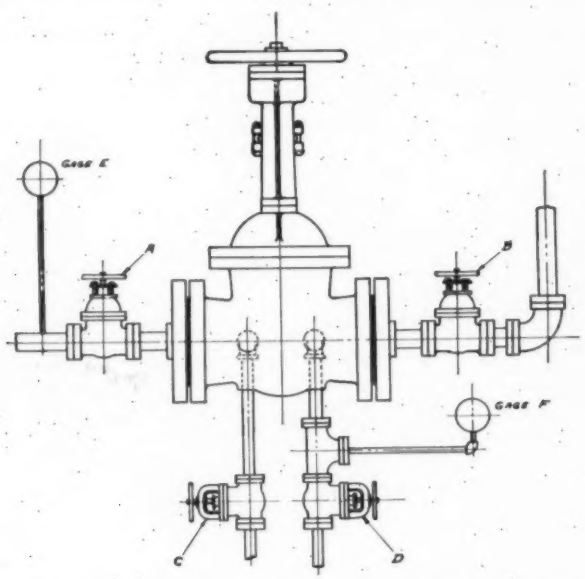

Fig. 12—Method of Opening 10-Inch, 400-Pound Code Valve in Conducting Valve Test.

was then turned off and the valve closed. Steam was again turned on with the valve closed, and the valve was left standing for 5 minutes to determine its tightness. This was done by gage "F". If the valve was tight on the initial test, it was then subjected to a number of cycles of opening and closing under full pressure and temperature. Each cycle consisted of an opening and a closing of the valve, and when one side of the valve had been tested, it was turned over and the opposite side was then tested. The following tabulation shows the result of this test on both sides of the valve for the number of cycles indicated in the first column:—

No. Cycles	Time Valve Allowed to Stand	Pressure on Gage "F"
1	5	0
1	5	0
1	5	0
2	5	0
5	5	0
10	5	0
10	5	0
20	5	0
25	5	0
25	5	0

The discharge flange was then removed with full pressure on

the inlet side and the valve was examined for leaks around the rings. The condition of the seat was also examined. The valve was allowed to cool all night and was then reinstalled on the following morning, the result of test on the opposite side being as follows:—

No. Cycles	Time Valve Allowed to Stand	Pressure on Gage "F"
5	5	0
10	5	0
10	5	0
25	5	0
25	5	0
25	5	0

The discharge flange was then removed and the valve was examined as before. The bonnet of the flange was then removed and the gate taken off for further examination. The disk showed no cutting of any kind and was in a very highly polished state, indicating that the valve could have been operated continuously for a large number of times without leaking. The pressure on both sides of the valve during test was 350 pounds and the total temperature of the steam varied from 750 degrees Fahr. on the first day to 770 degrees Fahr. on the second day. The unit pressure on the disk was approximately 1500 pounds per square inch.

After an examination of the condition of the valve at the end of the test which was extremely severe, it was concluded that the following conditions must necessarily be maintained if valves of lasting quality are to be used:—

1. Material used in seat rings and plug rings must be of sufficient hardness to withstand abrasive or wearing action when the valve is seated.
2. Material used must be of a character that does not seize or gall.
3. Material for very high temperatures, such as were encountered in the above test, must have the property of retaining its hardness.
4. The unit pressure on the seat ring and the plug ring should be carefully considered since pressures in excess of 1500 pounds per square inch would seem to be unwarranted from the test made.
5. It is possible to obtain a valve which, during its ordinary life, will be capable of closing and opening an indefinite number of times under full operating pressure.
6. Where high temperatures are encountered, materials having

low Brinell hardness will not stand up for any length of time without cutting.

Similar tests were carried out on valves trimmed with monel metal, monel metal against stainless iron, and valves fully trimmed with stainless iron, with the result that these valves failed early in the test.

Several other instances may be cited in connection with actual service of valves in high temperature high pressure installations. For instance, an overload valve in a large steam station was trimmed with hardened stainless about 360 Brinell and after about thirty operations or ten days the valve disk was cut severely and failure resulted. Fig. 2 is a photograph of this valve disk. The same valve trimmed with nitrided steel after one year's service is still functioning satisfactorily. Recently this valve was taken down for examination and it was found to be in as perfect shape as the day it was placed in service.

In a large oil refinery handling slurry, which is fuller's earth mixed with water, the abrasive action of this emulsion was such as to completely tear the seats and disks of valves away in about two weeks. Nitrided steel replaced previous metals with the result that valves have been in service more than one year without failure.

There are numerous other instances which may be cited as to the exceptional service of the material on the most severe work, and it might be well to note that the gate valves as used in all the 1400-pound pressure steam stations constructed during the past year have been mounted with nitrided steel.

Furthermore, the valves used in an experimental steam station in which temperature ranges were from 930 to 1100 degrees Fahr., were trimmed with nitrided steel, and the results of the experiment were such that a steam unit is now being constructed.

Conclusion

The author believes it unnecessary to do more than to describe the severe service in which nitrided steel has been used successfully, as the authors of the several other papers have described in detail methods and tests.

GENERAL ORAL DISCUSSION

G. M. EATON: On a first skimming of these papers on nitriding the first point that impressed itself upon the writer was the remarkable parallelism of effort that was followed in some cases. We cannot avoid making the suggestion that industry's money would be tremendously conserved if some higher authority could subdivide the subject and parcel it out sending to this, that and the other man the part he is best fitted to handle. Then let each man come back with his results and when he seems to really find something let others pitch in and prove whether he is right.

The next and only other point; I would like very much to ask each of the authors who made comparisons of nitriding steels on how many duplicate check tests he based his conclusions. I found only one statement along this line. Dr. Homerberg mentioned in connection with his Charpy tests that he made one check test. The others say nothing about it. We have learned in our nitriding development that when we thought we had found something, it was wise to repeat and repeat and repeat before we had a right to be sure that our finding was real. I strongly suspect, gentlemen, that no one is in a position to run one or two tests per type on a wide range of alloy steels and on this narrow basis put them into 1, 2, 3, order of excellence as nitriding steels. I believe any of the investigators can take one of several kinds of steel and run, say, 25 nitriding treatments presumably all identical and find greater variables than are shown in the entire ranges that have been given in the papers today as covering a variety of steels.

V. O. HOMERBERG: I wish to elaborate on the remarks made by Mr. Sergeson concerning the protective effect of tin. To those who are not acquainted with the application of protective agents against nitriding, the use of tin may appear to be questionable since it has a melting point below that of the nitriding temperature. However, it is entirely suitable provided certain precautions are taken. Parts to be protected should be cleaned, then dipped into molten tin or solder and kept there for a time sufficient to heat the parts somewhat so that the coating will not solidify immediately on the removal of the parts from the bath. The excess material can be shaken off or removed with a wire brush. If this precaution is not observed, particles of molten tin or solder will drop onto articles at a lower level in the nitriding box to produce soft spots. The amount of tin or solder which can be held by surface tension is all that is necessary to provide ample protection.

Mr. Sergeson in his bibliography refers to an article which I wrote a short time ago for a semi-technical journal. A column and a half on "The Limitations of Nitriding" were added without my sanction or knowledge. This discussion contains many mis-statements. Although an apology appeared in the next issue of the magazine, I wish to mention this fact in order that there may be no misunderstanding as to the source of this misinformation.

In reply to Mr. Nelson's inquiry Mr. Sergeson answered it from one

angle. Another cause of failure may be attributed to the sinking of the case because of the lack of requisite hardness in the core. A steel which possesses excellent core hardness has been developed and is being tested at the present time. Although it does not nitride so deeply as aluminum-chromium steel, it shows a core hardness not lower than 650 Brinell after the nitriding operation.

Mr. Tour has made some very valuable comments, especially with regard to the use of nitrided material to withstand the action of molten aluminum. His remarks pertaining to the softening of the nitride case by a long exposure at a certain temperature are of value since this question is of considerable importance. I believe that the softening effect is due to the diffusion of the nitrogen since the hardness at any given point is dependent upon the nitrogen concentration at that particular point. The results given in the paper by Dr. Walsted and me include hardness values obtained after reheating for an hour. Up to a certain point the greater the length of time of exposure at a given temperature, the greater will be the amount of diffusion. The marked softening effect mentioned by Mr. Tour may be attributed to the long exposure at the stated temperature to produce maximum diffusion of the nitrogen.

Dr. Waterhouse has just asked me as to the reasons for reheating nitrided material since such a procedure is not followed in actual practice. Dr. Walsted and I have conducted the reheating experiments to show the manner in which the structure of the case is altered with the reheating temperature. These experiments show the stabilizing effect of the aluminum on the nitride, the refinement of the structure of the case after reaching a certain temperature and the failure to coarsen this structure by reheating to higher temperatures, a fact which may be attributed to the inhibiting effect of the nitride particles to grain growth.

Mr. Eaton has made a valuable suggestion regarding duplication of effort. In order to avoid duplication of efforts in the investigation of the various phases of the nitriding problem, a nitriding committee of the A. S. S. T. has been formed of which I happen to be the Chairman. On this Committee are Messrs. Eaton, McQuaid, Snyder, Sergeson and Osterman. I think that you will agree with me that the members of this committee are well qualified to study this increasingly important problem. It will be our aim to present, at Convention time, up-to-date information on the subject.

I wish to inform Mr. Merten that the largest consumer of chromium-aluminum nitriding steels in the United States obtains a 0.030 inch case in ten hours.

JAMES C. NELSON: The question I want to ask is, is it possible to use nitriding steels for drawing or forming dies? So far I have heard no reference to tools of this kind. All references to applications have been where it was used for revolving or sliding machine parts such as gears, camshafts, worms, etc. No mention has been made of using it for tools. We use a large number of small drawing or forming dies where a small

amount of wear means throwing these dies away. Can nitriding steels be used for tools of this kind?

SAM TOUR: I would like to discuss briefly the general subject of nitriding and also several of the papers that have been given on nitriding. Mr. Sawyer brought up the question of just when nitriding of steel was first reported. He referred to some work of his in 1921. During the war, the Nitrate Division, Ordnance Department, U. S. Army constructed a plant at Sheffield, Alabama, for the manufacture of synthetic ammonia by the Haber process. One of the main difficulties in the Haber process was the breakdown of the reaction chamber due to the action of ammonia on steel. Immediately after the war the Ordnance Department started a very active study of this reaction. It was my good fortune to be in charge of this work. In 1919 and 1920 we studied steels not from the standpoint of getting a steel which would react easily and develop this excessively hard surface layer, but with the view towards finding a steel which would resist the reaction. Such a steel was needed in the reaction chamber. In that work we studied quite a number of steels. Some of the work was published later by J. S. Vanick. We noted at that time that the surface layer formed as the result of the action of ammonia on steel was very hard. We saw only the disadvantages of this layer and failed to see the possibility of a useful application of it. Obviously, it was very interesting a few years later to see that somebody had found a useful purpose for this thing that we were trying to get around.

With regard to Dr. Homerberg's paper, and his remarks regarding heat treatment after nitriding. He showed photomicrographs and stated that nitrided specimens still had Brinell hardnesses of 600 to 800 after heat treating to temperatures as high as 1900 degrees Fahr. In similar test work which I have done on aluminum-chromium steels after nitriding, I have found invariably that the case was much softened by heat treatment, indicating that there is a breakdown of the nitrided case. I have found that the nitride case breaks down and softens at the hardening temperature for these steels, namely, 1600 degrees Fahr.; that it softens at 1300 degrees Fahr. when heated for some length of time, one or two days; and that it breaks down when repeatedly and rapidly heated and cooled from between 600 or 700 degrees Fahr. and 1300 or 1400 degrees Fahr. This condition developed in small cores used in dies for die casting where nitrided steel showed a decided softening of the nitrided case within a week or two of service. I do not offer an explanation of what takes place, but simply offer this information for what it might be worth.

Dr. Fry, in his paper this morning, called attention to the effect of impurities in ammonia. I would like to add a little word to that, and that is the effect of impurities that are not originally in the ammonia but which are introduced in some manner in the process. For example, impurities picked up from ordinary garden hose used to make the connections between the ammonia tank and the tubes leading into the furnace, might cause trouble.

The unsolved problem of the theory of nitriding was touched on

briefly by Dr. Fry. I would like to suggest a method of attack. The work which I referred to before as being carried on by the Ordnance Department was also work in connection with catalysts for the reaction of nitrogen plus hydrogen to form ammonia. In that work it was found that iron was the best base for the catalyst. Certain additions to the iron were found valuable and others detrimental. The indications are that those things which poison the catalyst, for the manufacture of synthetic ammonia would be things that should not be added to nitriding steel. Those things that improve the catalyst, for the ammonia process should be desirable additions to steel for nitriding. In support of this, aluminum was found to be one of the beneficial things in the catalyst, and it proves to be beneficial in nitriding steels. Molybdenum was also found to be an aid. Carbon was found to be a poison to the catalyst, however, chromium in sufficient amounts was found to counteract the effect of this carbon. The poisoning action of carbon is probably the explanation of the impossibility today of nitriding cast iron. I would like to suggest along this line that further tests be run on developing steels based upon knowledge available of the effects of various materials on catalysts in the synthetic ammonia process. It might be very difficult to get some of these elements such as sodium, and potassium into steel but other elements such as titanium and uranium assist the catalysis and might be used in steel.

R. G. Roshong: I would like to make a few remarks on the nitriding process from the standpoint of production. I am very much interested in the remarks made by Mr. Tour concerning the softening effect on nitrided samples. There must be some critical range between the temperature of 1150 and 1350 degrees Fahr. which causes a softening of nitrided specimens. We have installed on a die casting machine, a core about 12 inches long which has been nitrided for a period of 25 hours. This core has been in service for about 6 months and is still "file hard" after producing over 40,000 castings from an aluminum-silicon alloy, shot into the die at 1150 degrees Fahr.

I would like to further comment on the supply of nitrogen for this process. There have been times in our production work when rather uncertain results have been obtained. Excessive amounts of ammonia have been used to obtain the proper results. In order to further study the effect of the amounts of ammonia used, the unfilled retort, which is 13 inches by 7 inches by 4 feet long was heated to a temperature of 1400 degrees Fahr. and the ammonia allowed to pass through it slowly for 36 hours with a dissociation of about 70 or 80 per cent. After this treatment an interesting thing was noted. The consumption of ammonia to obtain the proper results was materially cut down. I will not attempt to explain this phenomenon, but it appears to have a certain effect on the interior of the retort which is beneficial.

With regard to removing the troublesome hydrogen, it occurred to the writer that this might be done by the addition of some gas which would unite with the active hydrogen to form on inactive material. Some experiments were carried out with acetylene, believing that the acetylene might

unite with the hydrogen to form such products as ethylene or ethane. Much to our disappointment the acetylene quickly clogged up the iron gas-entrance tube to the retort with carbon. Upon repeating the experiment in the laboratory with glass apparatus this did not occur. There was no deposit of carbon. No further work has been done of this nature, upon the advice of authorities on the properties of acetylene, because we understand acetylene is quite explosive in certain combinations with air, and particularly so in the event that there is any copper present in the chamber which it is passing through, and, unfortunately, we have copper plated rivets in the retort.

E. J. P. FISHER: I would like to ask whether any of the speakers of the day have recently investigated the comparative wear resistance of nitrided steels and chromium-plated steel wearing parts. About a year ago, in attempting to find a superior material for use in special mandrels for the fabrication of curled hollow rollers from strip steel, such a comparison was made, the results of which may be cited here.

The mandrels were about 5/8 inch in diameter and about 18 inches in length, and were mounted in a special Baird forming machine. The strip steel being curled into the rollers varied in analysis and was about 3/32 inch thick and 5/8 inch in width, cold-rolled and annealed. This strip would also vary in hardness, due to presence or absence of decarburized "bark". Hence, an ordinary tool steel mandrel, properly hardened, would either be abraded by the "hard" strip or it would gall or pick up particles of the bark of "soft" strip. The average life of a good tool steel mandrel was approximately 12,000 pieces of curled strip. It was hoped that both nitriding and chromium-plating would give the required super surface hardness with suitable core toughness.

Heat treated and nitrided aluminum-chromium mandrels, first tried, failed by flaking due to decarburization prior to nitriding.

In the meantime, tests were run on a dozen mandrels made of S.A.E. 2315 steel, case-hardened and chromium-plated to about 0.0015 inch plate. These mandrels stood up exceptionally in the curling of both "hard" and "soft" strip. Galling was eliminated and abrasion decreased to such an extent that their average life was about 150,000 pieces of curled strip, per mandrel.

Finally, another set of nitrided aluminum-chromium steel mandrels were produced, these being satisfactory with regard to quality of the steel and the nitrided case. However, these mandrels only had an average life of 65,000 to 75,000 pieces of curled strip, due to both galling and lower wear resistance.

While the excellent results obtained with chromium-plated mandrels have been duplicated since the initial trials, some slight difficulty has been experienced due to a few instances of peeling of non-adherent plate. Worn mandrels have been replated with chromium, reproducing the desired diameter, thereby rejuvenating the original base.

Of course, there must be instances where chromium plate will not compete with nitrided steel. For uniformity of plating, the application of

chromium is limited to articles of simple contour, at least for the time being.

Again the question, "What has been your experience with regard to the relative hardness and wear resistance of these materials?"

W. J. MERTEN: One of the authors mentions three distinct layers in a nitrided case of chromium-aluminum steel on nital etching.

Our work suggests that the alloying elements chromium and nickel must play a part in this distribution of the crystal aggregates. This joining is entirely absent in the molybdenum-aluminum alloy nitrided and is present even at a 20-hour exposure of chromium-aluminum steel at 975 degrees Fahr. Our tests show that the outer layer is the hard nitrided case, the middle layer is a zone in which a dilution of carbon has been effected, due to carbide migration, but not actual decarburization. The third zone is a carbon enriched band and a spheroidal carbide aggregation can actually be observed. The phenomenon seems to have much in common with the dispelling of iron carbide from phosphide rich areas in plain low carbon steels and the concentration of pearlite bands or areas adjacent to iron phosphide streaks or patches.

SAM TOUR: On this question of further applications of nitriding steels I would like to suggest one other possible application. It has been mentioned that nitrided steels resist corrosion better than ordinary steels. I have found on some tests, that nitrided steels also resist, to some extent, solvent action of molten metals. Aluminum, for example, attacks steel more rapidly than cast iron. Indications are that nitrided steel will withstand the solvent action of molten aluminum as long as the nitrided case stays sufficiently high in nitrogen concentration. I imagine that there are a number of similar lines of application for nitrided steels to withstand the action of molten metals.